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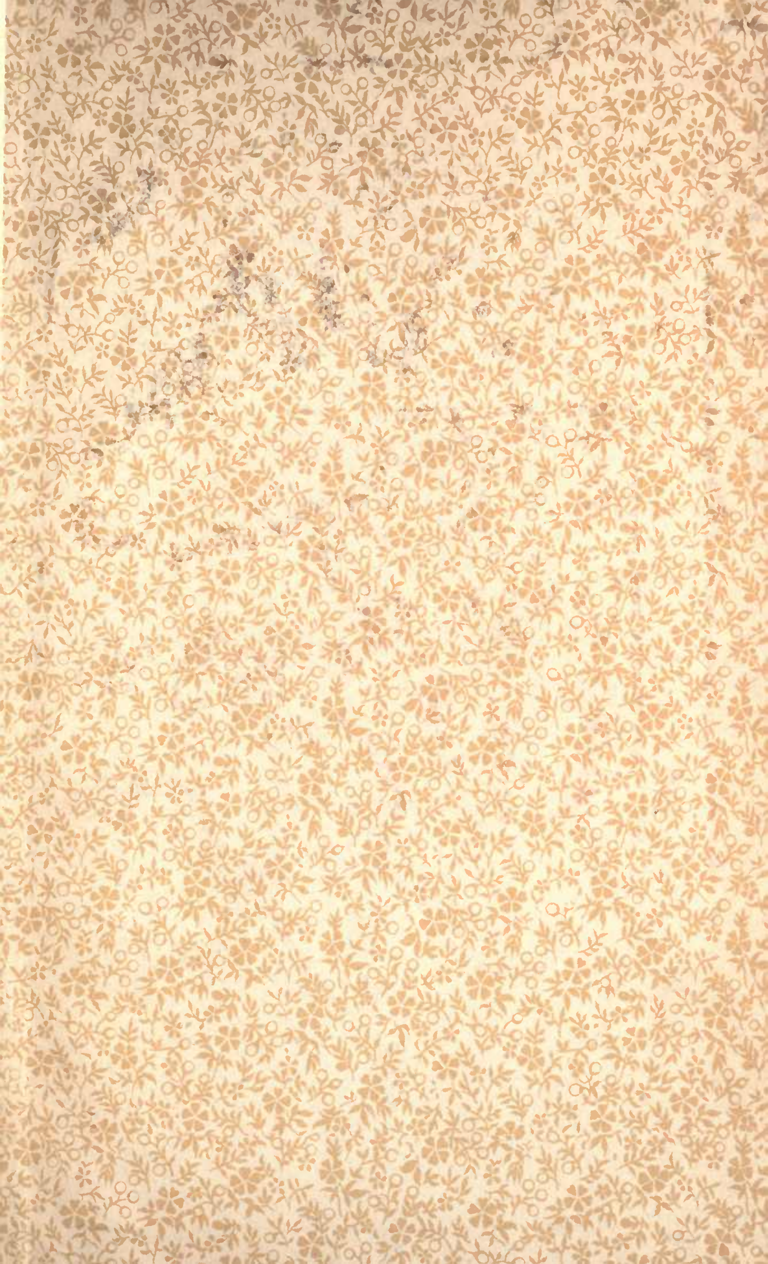

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Issued November 6, 1907.

U. S. DEPARTMENT OF AGRICULTURE. no. 47-5

BUREAU OF SOILS—BULLETIN No. 47.

MILTON WHITNEY, Chief.

CERTAIN ORGANIC CONSTITUENTS OF SOILS IN RELATION TO SOIL FERTILITY.

BY

OSWALD SCHREINER AND HOWARD S. REED,

ASSISTED BY J. J. SKINNER.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., June 10, 1907.

Sir: I have the honor to transmit herewith the manuscript of a technical paper entitled Certain Organic Constituents of Soils in Relation to Soil Fertility, by Oswald Schreiner, Howard S. Reed, and J. J. Skinner, of this Bureau. This article embodies the results of further experiments upon the effect of toxic organic substances upon soil conditions as indicated by the growth of plants in various cultures.

The material throws considerable additional light upon the question of soil fertility. In accordance with your suggestion it has been gone over carefully with Assistant Secretary Hays, who authorizes me to state that he concurs in my recommendation for its publication. This will form No. 47 in the series of bulletins of the Bureau of Soils.

Respectfully,

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

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CERTAIN ORGANIC CONSTITUENTS OF SOILS IN RELATION TO SOIL FERTILITY.

INTRODUCTION.

The poor qualities of unproductive soils are not always due to deficiency in nutrient mineral substances, but are often due to the presence of substances actually deleterious to plant growth. The presence of such deleterious substances may be demonstrated by the properties which the soil and its aqueous extract possess. When an unproductive soil is extracted with water, the aqueous solution is found to possess the properties of the soil itself, so far as plant growth is concerned; when a good soil is extracted, a good soil extract is obtained, and a poor soil yields a poor soil extract. The plant-producing power of soil extracts follows that of the soils from which they were made, almost regardless of soil texture or geological origin; where this is not the case the unproductivity is probably due to a poor physical condition, hardpan or poor cultural methods. In many instances poor soil extracts produce plants which are far less developed than similar plants grown in pure distilled water under identical conditions. This toxicity of the soil extracts has been investigated quite thoroughly and numerous experiments reported in former bulletins of the Bureau of Soils, using the plant as an indicator.

The toxic properties can be removed from a soil extract by a number of quite simple operations, such as treatment with carbon black, ferric hydrate, and other absorbent agents, whereby the toxic material is apparently removed from the solution. This action seems to be quite general for all poor soil extracts, although in other respects the properties of the soil extracts differ appreciably. The toxicity of certain soil extracts can be destroyed by merely boiling them. This may be due in some cases to a destruction and in others to a volatilization of the toxic agents, in which latter case the toxic properties can be found in the distillate. The toxicity can also be much weakened by dilution with pure distilled water, so that in the weaker solution there may even result a stimulation in growth such as that commonly observed with weak solutions of poisons. These toxic properties are also overcome in many instances by the addition of comparatively minute amounts of pyrogallol, naphthylamine, and other nonnutrient substances, a phenomenon which may be explained by assuming that these bodies have acted upon the toxic substance or have so altered the plant by stimulation or otherwise as to overcome them.

Another way of rendering the toxic properties innocuous is by the addition of certain of the fertilizer salts, as in practical agriculture in the field, or by the addition of calcium carbonate, which in the soil extract and in the soil itself is known to have very strong remedial properties where bad soil conditions exist. The addition of stable manure and green manure to the soil is also of the greatest benefit, as is well known in agricultural practice. Their beneficial action can not be entirely ascribed to the plant food or plant nutrients which these substances contain, but part of their action is due to the organic compounds which they contain and the changes which they set up in the soil.

It is, of course, well known that toxic soil conditions can be brought about by excess of salts or the presence of unfavorable inorganic compounds, such as ferrous iron, etc., but the properties of the toxic bodies causing unproductivity in ordinary agricultural soils under what might be termed normal conditions of continual crop culture, point strongly to the fact that the toxic bodies are organic and that the productiveness of a soil depends largely upon the condition of the organic matter in the soil and the processes which are at work in destroying the plant remains.

These toxic bodies, as shown in a former bulletin, may arise as the direct result of plant growth. When one crop succeeds another the soil is frequently rendered unfavorable for the support of a second crop of the same kind, even when the plants are only allowed to grow two or three weeks from the seed and can hardly have taken up enough plant food to have exhausted the supply naturally contained in the soil. Furthermore, the addition of plant nutrients to such a soil is not able entirely to overcome these toxic conditions for another crop of the same kind if immediately planted. They may, however, be overcome and the growth actually increased by the application of lime and green manure, either singly or in combination. The unfavorable conditions brought about by the excretion of material from the roots of the plant may affect the succeeding crop if immediately planted. When these plants are of a like species, such as wheat succeeding wheat, the effect is very marked. However, when cowpeas or corn is followed by wheat there is almost no detrimental effect, but when a closely related species like oats is used as the preceding crop the effect is again marked, although the retardation is not so great as when wheat follows wheat.

This same bad effect of root excretions is also shown by the effect of trees on wheat growing in conjunction with them, and is further illustrated by the poisonous effect which grass roots sometimes have on apple trees when sod is allowed to form in orchards.

Seeds will also throw off toxic substances during the process of germination which are detrimental to the growth of another crop of the same kind of seedlings, if planted before the unfavorable conditions have been ameliorated by treatment or by natural processes, such as oxidation or decay.

The beneficial effects of mineral plant nutrients and of organic manures are too well known to require more than brief mention in this place. When soil conditions are favorable for the decomposition and humification of organic material a marked increase in plant growth results. Numerous experiments showing this beneficial action have been described in Bulletins 28, 36, and 40 of this Bureau. A single experiment may be described in this place to illustrate the principle of this action.

Green cowpea vines were added to a poor soil at the rate of 5,000 parts per million of soil. The soil was kept at optimum water content and frequently stirred during the next twenty-six days. As decomposition progressed the soil developed an odor like that of decomposed stable manure. At the end of twenty-six days green cowpea vines were added to another sample of the same soil in the same proportion as originally applied. Both the samples of soil were then immediately extracted with distilled water, and the extracts used as a medium for growing wheat plants in comparison with the extract of a sample of soil to which no cowpea vines had been added. At the end of eleven days the growth produced in each set of solutions was measured by taking the green weight of the plants. Representing the growth of the plants in the extract of untreated soil as 100, the growth in the extract made immediately after adding cowpea vines was 95, and that in the extract of soil in which cowpea vines had stood twenty-six days was 130. This shows that the application of green manure was able to produce an increased growth, amounting to 30 per cent where the plants grew so short a time as eleven days, provided that the green manure had had sufficient time to decompose.

The toxic properties of soils have been demonstrated and the existence of toxic bodies is a reality with which it is necessary to deal in future soil studies on the fertility and infertility of our agricultural lands. A very important phase of work in these soil studies yet remains to be done before a thorough knowledge of these bodies can be obtained and the best means of treatment to overcome them established. Many of their properties have already been determined, so far as they relate to plant growth. Not only have their physical properties been studied, but the physiological properties, their effect on the growth and nutrition of plants or other physiological functions, have also been ascertained for many soils. It remains to make a closer study of the chemical properties of these toxic bodies and to isolate them from the soil.

PROPERTIES OF THE ORGANIC CONSTITUENTS OF SOILS.

The problem of isolating organic bodies from soils has been attempted from time to time in the history of agricultural science. Braconnot, Walser, Gyde, and others even attempted to show by chemical means the presence of the toxic excretions of plants, and it is largely due to their failure to obtain positive reactions that the matter was dropped for many years. Investigations have been reported from time to time on the isolation of various humic acids, crenic, apocrenic, ulmic, etc., but the composition of the acids isolated has been a most variable one, differing with each investigator and with each method employed. It would not be far from the truth to say that none of these acids have been shown to exist and that we know almost nothing about their chemical composition or constitution.

The work of isolating and studying the nature of such bodies is now in progress, but it is necessarily slow and difficult to accomplish. In the first place, the amount may be very small, and, secondly, the composition of the organic matter of the soil is undoubtedly very complex, being made up of many individual organic compounds. The absorptive power of the soil for organic bodies is so very great that the ordinary solvents, such as water, alcohol, chloroform, etc., take out but very minute amounts of organic material, although this material may be quite soluble when not associated with the soil. The amounts of organic matter in ordinary soils is really appreciably large, the average content being as high as 2.06 per cent for the soil and 0.83 per cent for the subsoil, as found in thousands of samples from all parts of the United States, covering in all 237 types of soil. It is obvious that this organic matter is of very complex composition, as its properties are quite different in soils from different localities. The amount of nitrogen also is considerable, as much as 0.1 to 1.0 per cent, and when we consider that only a small amount of this nitrogen is in the form of ammonium compounds or nitrate and that the larger amount is in organic form it is obvious that the problem is a very complex one, but one of great agricultural importance.

In view of the difficulties which are encountered, and must be encountered for some time, in the isolation of these bodies by purely analytical methods, it was thought that the synthetic way of adding bodies of known composition, known properties, and known derivation from plants to culture media, in order to study their properties and the effect which they might have upon plant growth, would answer the question whether such bodies are toxic to plants much sooner than could possibly be done by first isolating them from the soil and then trying their properties. Proceeding in this synthetic manner, it is possible to reach a broader survey of the effect of organic plant remains and get a clearer conception of the manner in which these function in the soil.

Plant remains contain such organic compounds in their tissues as we have studied, hence it is not improbable that these exist in the soil as such, or as decomposition products, or as compounds formed from them by the action of aerobic and anaerobic micro-organisms. Prominent among these organic compounds would be the carbohydrates, proteids, and lecithins which exist in the living cells of every plant. During the decay of these complex organic bodies a large group of what are known as primary degradation products are formed and from these, secondary decomposition products may result.

Many of the normal decomposition products of proteids, such as leucine, asparagine, etc., are not toxic, but appear to serve as direct nutrients for the plants, but others, like tyrosine and products resulting from it, are inhibitive to plant growth. When proteids decompose under unfavorable soil conditions they may give rise to substances more toxic than the original; for example, phenols, cresols, and aromatic acids, which may also result from tyrosine. Choline, a decomposition product of lecithin, is moderately toxic to plant growth, but stimulates in low concentrations. Neurine results from the action of bacteria on choline and the widely distributed lecithin, and is moreover quite inhibitive to plant growth.

The cumarin mentioned below as occurring in certain plants and quite inhibitive to plant growth may also be formed from carbohydrates by the action of certain mold fungi. One of the fungi which occurs in certain soils has the ability to produce quinone from proteids. Small amounts of this quinone are harmful to plants and may injure growth unless it is converted into some harmless substance.

A fungus which causes decay of wood has the ability to form vanillin. This substance, which is toxic to plants, is commonly regarded as of rare occurrence, but is found in a number of common plants, and its derivatives may form a part of the organic constituents of the soil.

The presence of pyridine and related bodies in soils is rendered not only possible but extremely probable by recent soil investigations. Hence a study of their properties is of value in relation to soil conditions, and in general it may be said that pyridine and its compounds are distinctly toxic to plant growth.

Again, such substances as the terpenes are of interest in this connection because of their probable presence in soils. In general, it may be said that terpene compounds are inhibitive to plant growth. One of the terpene derivatives, borneol, which is quite toxic to plant growth, occurs in pine needles and in the common golden-rod. The terpene compounds are widely distributed and are to be regarded as plant excretions. Their introduction into the soil is almost inevitable through the decay of plants, many of which are agriculturally classed as weeds and known to contain terpene bodies. Since the terpene bodies, as is well known, are antiseptics, they would not themselves be materially altered by micro-organisms of the soil, although many of them are subject to oxidation. They would, therefore, be likely to persist in the soil in one form or another for some time. The presence of terpene derivatives in the soil is therefore more than probable and where they are persistent they may affect the growth of plants on that soil.

It has been demonstrated by the studies described in this bulletin that substances commonly used as fertilizers in agricultural practice have in addition to their function as plant nutrients a well-defined power to overcome and actually destroy toxic bodies. Substances like nitrate of soda and lime, acting in cooperation with the activities of the plant roots, are able to destroy or render harmless various organic substances which previously had a toxic effect on the plants. This fact is believed to be of distinct value in the study of soil problems, because it is known that many cases of infertility are simply due to the presence in the soil of compounds having a toxic action upon plants. When such soils are extracted with water the solution when used as a medium for plant growth displays many of the same characteristics as are displayed by solutions of the organic compounds described in this bulletin. Such toxic soil extracts may be greatly improved by the addition of fertilizer substances, but up to the present the method by which amelioration was brought about had not been demonstrated. It had been distinctly shown, however, that amelioration was not due to the addition of plant nutrients, since equal, if not greater, improvement resulted from treatments which added nothing in the nature of plant nutrients. The present investigations become of value, therefore, in showing that fertilizer substances have a power to act destructively upon deleterious organic compounds, especially when associated with the activities of growing plants.

Tyrosine, one of the degradation products of the proteids, has been found unfavorable to plant growth, a fact which is believed to shed light upon the first effects of green manures. When tyrosine is darkened by oxidation, it is changed in a manner analogous to the changes which occur during the decomposition of green manure. The dark-colored solution that results from the oxidation of tyrosine is highly beneficial to plant growth and acts like an extract of well-rotted stable manure. Processes like this may occur during the decomposition and humification of organic matter in the soil.

The beneficial effects of processes which involve oxidation are well illustrated by the effects of neurine, choline, and betaine. Neurine, which is very toxic to wheat plants, is not a highly oxidized compound. Choline is more highly oxidized than neurine and is less toxic to plants. Betaine, which is still more highly oxidized than choline, is not at all toxic to plants in concentrations of 1,000 parts per million or less.

It is therefore readily understood how processes of oxidation may improve soil conditions when we know that toxic bodies like choline and tyrosine are converted into nontoxic bodies by oxidation. When the soil possesses the proper amount of water and a proper physical condition, it is possible for changes to occur in the organic constituents, which changes, commonly known as "humification," result in beneficial products. When the soil is saturated with water or is so packed that a sufficient supply of air is not afforded, then the organic matter may be differently decomposed, giving organic compounds in a low stage of oxidation which are unfavorable to plant growth, and bring about toxic conditions which temporarily restrict the productivity of the soil. When certain plants are used as green manures it has been found unwise to plant a given crop immediately, because their effect upon plant growth is not beneficial. After sufficient time has elapsed for decomposition to go on a beneficial effect is produced by such green manures. The immediate harmful effect is presumably due to the presence of bodies like tyrosine, cumarin, and their derivatives. Cumarin, which also has properties toxic to plants, is the odorous principle of many sweet-scented grasses and clovers. Processes of oxidation, which are known to occur in all fertile soils, convert such vegetable substances into beneficial humus like bodies.

THE EFFECT OF VARIOUS ORGANIC SUBSTANCES OF VEGETABLE ORIGIN.

Continued study of the phenomena exhibited by poor soils has shown that the deleterious properties are often due to the presence of toxic organic compounds. Accordingly, it seemed profitable to investigate the properties of a number of organic substances of vegetable origin with relation to the growth of higher plants. Many of the substances tried have been studied by others as sources of nutrition for bacteria and fungi, but the effect upon the higher plants has not been so extensively studied.

METHODS.

The experimentation consisted in studying the effect of a number of organic compounds upon seedling wheat plants grown in solutions. The compounds employed were, unless otherwise stated, the purest preparations obtainable upon the market.

The water used in making solutions was the ordinary laboratory distilled water treated with carbon black. This treatment makes the distilled water a good medium for plant growth, as was demonstrated in Bulletin 36 of this Bureau.

The experiments upon the action of various organic compounds upon plants were conducted with the pure preparations dissolved in carbon-treated distilled water. Whenever possible, the highest concentration employed was 1,000 parts per million.

The concentrations of the individual compounds were usually 1,000, 500, 250, 100, 50, 25, 5, and 1 part per million, but a number of the compounds used were soluble only in quantities less than 1,000 parts per million, and in these cases the range of concentrations was much smaller. Such instances are noted in the last column of Table I.

The wheat was germinated according to the method described by Livingston,[a] and in Bulletin 40 of this Bureau. The seedlings were put into the cultures at the stage when the first true leaf was beginning to emerge from its sheath. Salt-mouth bottles, having a capacity of 250 c. c., were used as culture jars, and ten wheat plants were grown in each jar.

Twenty wheat plants were used in testing each concentration and comparison was made always with an equal number of plants growing in carbon-treated distilled water under like conditions. During the seasons of the year in which the conditions for growth were the best, each experiment was continued for from eight to ten days, but during the cloudy winter weather some of the experiments were continued for twelve or fourteen days; the exact length of time for each experiment is given in the third column of Table I.

The experiments were always set up in duplicate under such conditions that individual variations could be eliminated. A brief survey of the plan of the experiments makes it evident, furthermore, that each culture in any given series constituted a control for the other cultures of that series. In addition each series was repeated several times, always in duplicate, according to the plan of procedure used for the first series. It is obvious that in this way each fact is really established by a large number of properly controlled experiments and that the separate experiments become, on this account, a control one upon the other, thus forming a network of experiments, all showing the same general action.

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[a] Livingston, Plant World, 9, 13 (1906).

Two, and sometimes three, criteria of growth were employed, viz, transpiration, green weight, and turgidity. No one of these criteria can be regarded as absolute, but they usually agreed in indicating the order of results, which was the point sought for in these experiments.

Transpiration, since it is proportional to the growth of leaves and roots, is a criterion capable of quite general application. The close relation between transpiration and the other reliable methods used for measuring growth has been shown by the investigations of Livingston[a] and Jensen.[b]

The weight of the tops or of the entire plants in the fresh condition was also taken as a measure of their growth and as a means for comparison with the control plants.

The condition of the root tips was also noted as an aid in determining the lethal concentration. When killed the root tips lose their turgidity and soon become slimy. Before this ensues they generally show indications of injury by discoloration in the region occupied by the most actively growing cells, or meristem. In some solutions the tips stop elongating and become swollen, simultaneous with more or less discoloration.

The photographic reproductions, Plates I to VI, show in a general way the relative growth of the plants in comparison with their controls.

Many of the substances employed produced an effect mainly upon the tops, others affected mainly the roots of the plants. In computing the effects of these different treatments, the transpiration figures are believed to be a more reliable indication of growth of wheat in water cultures, as far as the entire plant is concerned, than the weight of the green tops. Transpiration is more nearly proportional to the growth of both roots and tops; while the green weight is not at all an indication of root growth, and is moreover liable to some error in indicating the actual growth of tops.

It is not to be inferred, however, that any one standard is an absolute measure of growth of wheat in water cultures, but when only one is used, transpiration appears to be much more accurate than the green weight of tops.

COMPOUNDS ARISING FROM PROTEIDS.

In the breaking down of proteid bodies there are formed a number of amido acids as intermediate products, which are more or less unstable. These substances not only appear in the decomposition of plant remains, but exist in very considerable quantities at the time of germination and in the seedling plant. These bodies are found in relatively large amounts in plants especially in members of the legume and mustard families, not only in the seedling stages of the plants, but also in the roots, rootstocks, stems, buds, and in all parts which store up reserve material for the nutrition of the plant. Since plants of these families are extensively used in the practice of green manuring they may become important soil constituents.

---

[a] Livingston, B. E., Bot. Gaz., **40**, 178 (1905).

[b] Jensen, G. H., Bot. Gaz., **43**, 11 (1907).

According to Dojarenko,[a] the amido-acid nitrogen forms a very considerable portion of the nitrogen in humus bodies (22 to 70 per cent). S. Suzuki,[b] in studying the formation of humus, was able to show by the decomposition products obtained that proteid bodies were present. He was able to show the presence of alanine, leucine, amino-valerianic acid, proline, aspartic acid, glutaminic acid, tyrosine, and histidine among the decomposition products obtained by treating the so-called humus precipitate with hot concentrated hydrochloric acid.

Aspartic acid ($C_4H_7NO_4$) has been found in young sugar cane and in the molasses of the sugar beet.[c] It is probably not widely distributed in nature, but has been shown to exist in seedlings of the bean[d] and pumpkin.[e]

Aspartic acid was tested upon wheat seedlings, using concentrations ranging between 1 and 750 parts per million. The plants were killed in solutions stronger than 500 parts per million, presumably on account of the acid properties of the solution. In the solution containing 100 parts per million there was little injury, and below that no injury.

Asparagine ($C_4H_8N_2O_3$) is a water-soluble form of organic nitrogen material which is relatively abundant in plants. It was first found in the young shoots of asparagus and subsequently in a large number of other plants representing many different families.[f]

---

[a] Dojarenko, Landw. Vers.-Stat., **56**, 311 (1902).

[b] Bull. Coll. Agr., Tokyo, **7**, 513 (1907).

[c] Scheibler, Jahresb. Chem., 1866, 399.

[d] Mercadante, Ber. chem. Ges., **8**, 823 (1875).

[e] Schulze and Barbieri, Ber. chem. Ges., **11**, 710 (1878).

[f] Delaville, Ann. Chim., **41**, 298 (1802).
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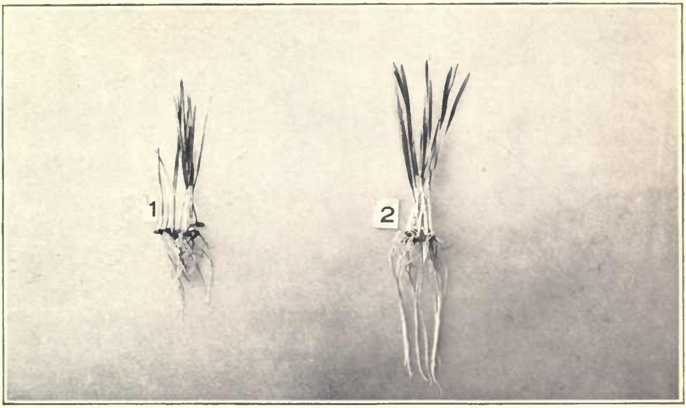

FIG. 1.—EFFECT OF FRESH AND DISCOLORED SOLUTIONS OF TYROSINE.

[Wheat grown in: (1) Freshly prepared solution of tyrosine, 16 parts per million; (2) discolored solution of tyrosine, originally containing 16 parts per million.]

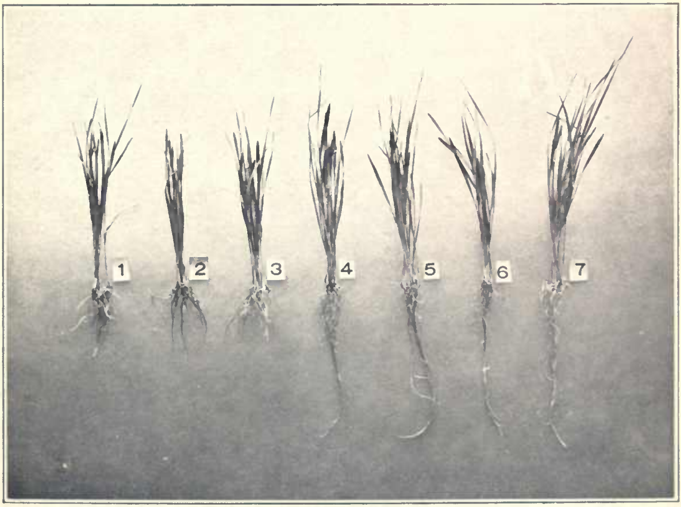

FIG. 2.—EFFECT OF CHOLINE, FORMED DURING THE GERMINATION OF SEEDS AND DECOMPOSITION OF VEGETABLE MATTER.

[Wheat grown in: (1) Control in pure distilled water; (2) solution of choline, 1,000 parts per million; (3) 500 parts; (4) 100 parts; (5) 25 parts; (6) 5 parts; (7) 1 part.]

Asparagine forms a good source of nitrogen for fungi,[a] and bacteria.[b] It is not toxic to higher plants in concentrations of 1,000 parts per million and less, which were used in our experiments. It appears to serve, as Nakamura[c] has also shown, as a nutrient for the higher plants, although Klebs,[d] found that a concentration of 1 per cent (10,000 parts per million) was sufficient to inhibit spore formation in a green alga.

Glycocoll ($C_2H_5NO_2$), amido-acetic acid, is one of the simpler proteid degradation products found where decomposition is occurring. It forms a moderately good source of carbon for bacteria and fungi,[e] but a 1 per cent solution was found by Klebs[d] to inhibit zoospore formation in the alga *Conferva minor.*

In our experiments with wheat seedlings glycocoll was beneficial to growth in a concentration of 1,000 parts per million and less.

Alanine ($C_3H_7NO_2$), or alpha-amidoproprionic acid, is of interest because of its relation to phenylalanine and tyrosine, two substances which are found in many plants. Alanine itself does not appear to have been found as yet in plants; it is known, however, as a very common splitting product of proteids. A solution of alanine containing 500 parts per million was slightly injurious to the roots of wheat plants; in weaker concentrations no injury whatever was shown, and in fact growth was improved.

---

[a] Mayer, Untersuch. über alkohol. Gärung. 1869.
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[b] Eijkman, Koch's Jahresb., 1892, 71.
Pere, Ann. Inst. Past., **6**, 512 (1892).
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Sullivan, Jour. Med. Res., N. S., **9**, 109 (1905).

[c] Bul. Coll. Agr., Tokyo, **2**, 466 (1897).

[d] Die Bedingungen der Fortpflanzung bei einigen Algen u. Pilzen, Jena, 1896.

[e] Loew, Chem. Energie d. lebenden Zellen, München, 1899, 69.
Laurent, Ann. Soc. Belge Micr., **14**, 29 (1890).

Tyrosine[a] ($C_9H_{11}NO_3$) is one of the most important and most widely distributed proteid hydration products. Tyrosine exists as such in many plant organs, especially those which contain appreciable amounts of proteid, and is to be regarded as a splitting product of proteid. It has also been found in certain fungi.[b] The proteids are bodies of exceedingly complex constitution and under the stress of artificial chemical treatment, or natural processes, the complex structure is partially broken down and the chief products of this splitting up of the molecule are amino-acids of the paraffin series, such as glycocoll, leucine, aspartic acid, glutaminic acid, arginine, histidine, etc., and compounds of the aromatic series, such as phenylalanine, tyrosine, etc. The tyrosine group appears to be present in the proteid molecule, and to it are due some of the reactions shown by this class of bodies.

Tyrosine in the culture bottles proved to have a very injurious effect upon wheat seedlings. At a concentration of 100 parts per million it killed the roots and injured the tops. It was likewise injurious in a concentration as low as 16 parts per million. During the first few days the roots showed a pathological condition, and before the tenth day they were entirely dead. At a concentration of 1 part per million there was a very slight increase in growth over the controls. The physiological action of different samples of tyrosine was not always of equal intensity.

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[a] For literature on tyrosine, see Reach, Virch. Arch., **158**, 288 (1899).
Schulze, Barbieri, and Bosshard, Zeit. physiol. Chem., **8**, 63 (1884).
Ritthausen, Die Eiweisskörper der Getreidearten, Bonn, 1872, 214.
Bleunard, Compt. rend., **90**, 1080 (1880).
Fleurent, Compt. rend., **121**, 216 (1895).
Gorup Besanez, Ber. chem. Ges., **10**, 781 (1877).
Schulze and Barbieri, Ber. chem. Ges., **11**, 710, 1233 (1878); Landw. Jahrb., **7**, 411 (1878).
Schulze, Ber. chem. Ges., **12**, 1924 (1879); Jour. prakt. Chem., **135**, 337 (1883); Landw. Jahrb., **12**, 909 (1883).
Meunier, Ann. agron., **6**, 275 (1880).
Wassilieff, Landw. Vers.-Stat., **55**, 45 (1901).
Schulze, Zeit. physiol. Chem., **30**, 277 (1901); Ber. bot. Ges., **21**, 64 (1903).
Schulze and Castoro, Zeit. physiol. Chem., **38**, 199 (1903).
Bertel, Ber. bot. Ges., **20**, 454 (1902).
Borodin, Bot. Ztg., **40**, 590 (1882).
Tollens, Verhandl. Ges. Naturforsch. Hamburg, **2**, 165 (1901).
Sack and Tollens, Ber. chem. Ges., **37**, 4115 (1904).
Orloff, Chem. Centr., 1897, I, 1234.
Schulze and Barbieri, Landw. Vers.-Stat., **24**, 167 (1880); Ber. chem. Ges., **12**, 1924 (1879).
Schulze and Engster, Landw. Vers.-Stat., **27**, 357 (1881).
Leitgeb, Mitteil. bot. Inst. Graz, 1888, 215.
Lippmann, Ber. chem. Ges., **17**, 2835 (1884).
Bamberger and Landsiedl, Monatsh. Chem., **25**, 1030 (1904).
Gonnermann, Arch. gesammt. physiol., **82**, 289 (1900).
Planta, Ber. chem. Ges., **23**, 1699 (1890).
Shibata, Jour. Coll. Sci., Imp. Univ., Tokyo, **13**, 329 (1900).

[b] Winterstein, Zeit. physiol. Chem., **26**, 438 (1899).
Winterstein and Hofmann, Hofmeisters Beitr., **2**, 404 (1902).
Bourquelot and Harlay, Bul. Soc. Myc., **12**, 153 (1896).

Since tyrosine is so widely distributed in plants and results so readily from the decomposition of proteids, it is highly probable that it and its decomposition products are present in soils, at least as intermediary products of plant decay in the formation of humus. Especially interesting in this connection are the numerous products, such as the aromatic acids and phenols, which are so frequently found during the decay of the proteids, and all of which, as Baumann[a] has shown, are probably derived from the tyrosine group in the proteid by oxidation and reduction processes together with the splitting off of water, carbon dioxide, or ammonia. Thus tyrosine ($C_9H_{11}NO_3$) by reduction can yield hydroparacumaric acid ($C_9H_{10}O_3$) and ammonia, and this in turn, by splitting off carbon dioxide, gives rise to p-ethyl phenol ($C_8H_{10}O$). By oxidation and splitting off of water this compound can yield p-oxyphenyl acetic acid ($C_8H_8O_3$), and on splitting off carbon dioxide, p-cresol (C_7H_8O),[b] which on further oxidation and splitting off of water yields p-oxybenzoic acid ($C_7H_6O_3$), and then phenol (C_6H_6O) and carbon dioxide.

All these products except the p-ethyl phenol are known as albumin decomposition products. Phenyl propionic acid and phenyl acetic acid, which are likewise albumin decomposition products,[c] can also result from tyrosine by successive degradation.

Bacteria seem to have the property of oxidizing tyrosine to ammonia, carbon dioxide, and water, as Hoppe-Seyler[d] has only found these substances as end products in proteid decay under certain conditions, tyrosine as well as leucine appearing only as intermediary products.

In Bulletin 40 it was shown that toxic soil conditions could arise as the result of the direct functioning of the plant. Since we know that the metabolic processes of plants are greatly affected by different conditions, it seems reasonable that under such conditions the character of the toxic excretions might likewise be changed, and show therefore widely different properties.

It is well known that when seedlings are grown under different conditions the composition of the mixture of proteid degradation products is markedly changed. Under certain conditions the usually large accumulation of asparagine in legume seedlings has been found to give way to excessive formation of tyrosine and leucine. Bertel[a] has shown that by excluding oxygen, and also under other conditions, larger amounts than are usually found of tyrosine accumulated in the cells of the roots.

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[a] Ber. chem. Ges., **12**, 1450 (1879).

[b] This has been shown to be toxic to lupines by True and Hunkel, Bot. Centr., **76**, 289 (1898).

[c] Salkowski, Ber. chem. Ges., **12**, 648 (1879); Zeit. physiol. Chem., **9**, 491 (1885). Kerry, Monatsh. Chem., **10**, 864 (1885).

[d] Zeit. physiol. Chem., **8**, 214 (1884).

These products of proteid degradation which occur in the processes of germination and plant growth are also largely affected by subsequent changes in the plants themselves, probably by the action of enzymes, oxidizing, and reducing the immediate degradation products of the albumin molecule, associated with a splitting of amido groups and carbon dioxide, giving rise to a very large number of possible decomposition products of these primary proteid degradation products. The study of the further changes which tyrosine can undergo in lupine seedlings by Bertel is a good illustration of such transformations. He demonstrated that the large accumulation of tyrosine in chloroformed seedlings disappeared after some time with the formation of homogentisinic acid and possibly its oxidation products, or at least with the formation of compounds giving reactions similar to those afforded by this acid. The proteid hydrolysis in plants is still too little understood to afford a clear conception of the processes which take place. Just what changes the primary hydration products undergo, and some of these changes are doubtless rapid, is but little understood, and it is evident that these metabolic processes of growing plants can not be studied without taking into consideration such secondary reactions as those mentioned above. It is to such secondary changes that the differences between the mixture of amino acids formed by artificial hydration processes from proteids and that found in plants must be ascribed. Tyrosine, which appears in the first stages of growth of the lupine seedlings in considerable amounts, is soon changed further by the enzyme tyrosinase, which is most plentiful in the upper portions of the roots. The homogentisinic acid, which results as the product of this reaction, accumulates according to Bertel under certain conditions, while under normal conditions further oxidation of this substance takes place in the youngest portions of the seedling roots.[b]

The nature of this change, as well as the end products, is still unknown. It is interesting in this connection that in the course of physiological stimulation (hydrotropism, heliotropism, geotropism) there is an almost universal transitory checking of this further oxidation of homogentisinic acid, causing a temporary increase of the latter in the plant tissues.[c]

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[a] Ber. bot. Ges., **20**, 454 (1902).

[b] In this connection see Schulze, E. Ber. bot. Ges., **21**, 64 (1903); Schulze and Castoro, Zeit. physiol. Chem., **48**, 387 (1906).

[c] Czapek, Ber. bot. Ges., **20**, 464 (1902); **21**, 229, 243 (1903); Jahrb. wiss. Bot. **43**, 419 (1906).

The action of tyrosinase on tyrosine, changing it to homogentisinic acid, carbonic acid, and ammonia with oxygen absorption, belongs probably to the most general processes of metabolism. Bacteria also produce tyrosinase, as was shown by Gessard[a] for *Bacillus pyocyaneus*, and by Lehmann[b] for other bacteria. Interesting in this connection is the appearance of guanidine in seedlings as found by Schulze[c] which probably results, through the action of such secondary changes as those mentioned above, from arginine.

Upon long standing with exposure to air the tyrosine solutions appeared to have undergone this same change, all of them having become quite dark in color. The changes wrought were probably the same as those produced by the enzyme tyrosinase, which oxidizes tyrosine to homogentisinic acid which in turn gives rise to the dark-colored compound.

An instructive result was obtained by studying the action of such a tyrosine solution which had suffered discoloration incident to age. The solution had become so dark in color that it resembled manure extract. It was diluted so that it was equivalent to a 16 parts per million solution of fresh tyrosine. This solution was used for growing wheat seedlings in comparison with a freshly prepared solution of equal strength.

In a few days the plants in the two solutions showed pronounced differences, which became greater as the experiment was continued. Plate I, figure 1, shows the appearance of the plants when the experiment was discontinued at the end of the twelfth day. The plants in the fresh tyrosine were more poorly developed than those growing in distilled water. The leaves were narrow and beginning to die at the tips; the roots were dead and had become slimy. The plants in the discolored tyrosine had made excellent growth. They resembled plants grown in manure extracts. The leaves were rich, green, broad, and making vigorous growth. The roots showed a similar good development. During the course of the experiment the plants in the fresh tyrosine had transpired 19 grams of water and attained a green weight of 580 milligrams. The plants in the discolored tyrosine had in the same time transpired 38 grams of water and attained a green weight of 940 milligrams.

These results are believed to have importance in explaining the value and action of the so-called "green manures." As previously mentioned, tyrosine and related compounds are quite widely distributed in the vegetable kingdom. They may even increase in number and in quantity when vegetable matter is allowed to decompose in the soil. Our experiments indicate that bodies like tyrosine and choline have a toxic action upon plants, but that these substances in a more highly oxidized stage are actually beneficial to plant growth. When first applied to the soil, green manures may exert a depressing effect upon the growth of the crop. After time enough has elapsed for the decomposition of the vegetable matter with change to other compounds, the crop shows a marked benefit from the action of the green manure.

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[a] Compt. rend. Soc. Biol., **50**, 1033 (1898).

[b] Münch. med. Wochenschr., **49**, 340 (1902).

[c] Ber. chem. Ges., **25**, 658 (1892); Zeit. physiol. Chem., **17**, 193 (1892); Landw. Vers.-Stat. **46**, 383 (1895); Zeit. physiol. Chem., **30**, 241 (1901); Ber. bot. Ges., **21**, (1903).

Leucine ($C_6H_{13}NO_2$), alpha-aminoisobutylacetic acid, is also a very common decomposition product of proteids. It also occurs in the fly agaric (*Amanita muscaria*), in vetches, lupine, gourd, molasses of the sugar beet, potatoes, blighted corn, etc. Laurent[a] found that leucine was a favorable nutrient for fungi. The effect of leucine upon wheat plants was studied by allowing the plants to grow in solutions having a concentration of 500 parts per million or less. The growth of the plants was uniformly benefited by the presence of leucine.

COMPOUNDS ARISING FROM LECITHINS.

Choline[b] ($C_5H_{15}NO_2$) is widely distributed in the vegetable kingdom, in seeds and the growing parts of plants. It is not related to the proteid bodies directly, but forms a part of the molecule of the organic phosphorus compounds of both plants and animals, the lecithins, and is therefore always found as a product of the decomposition of these bodies. According to the observations recorded in the literature, choline is also found in various plant tissues associated with lecithin, and it does not follow that it must always be considered as a lecithin degradation product.[a]

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[a] Ann. Soc. Belge Micr., **14**, 29 (1890).

[b] Schulze, Zeit. physiol. Chem., **11**, 365 (1887); **12**, 405 (1888); **17**, 140, 193 (1892); Ber. chem. Ges., **22**, 1827 (1889); Landw. Vers.-Stat., **46**, 383 (1895).

v. Babo and Hirschbrunn, Ann. Chem., **84**, 22 (1852).

Claus and Keese, Jour. prakt. Chem., **102**, 24 (1867).

Schmiedeberg and Harnack, Jahresb. Chem., 1876, 804; Arch. exp. Path., **6**, 101 (1876).

Griess and Harrow, Ber. chem. Ges., **18**, 717 (1885).

Boehm, Jour. prakt. Chem., **138**, 37 (1884); Arch. exp. Path., **19**, 60, 87, (1885).

Jahns, Ber. chem. Ges., **18**, 2518 (1885); **26**, 1493 (1893); **23**, 2973 (1890); Arch Phar., **235**, 151 (1897); **229**, 675 (1891); **225**, 479 (1887).

Brieger, Zeit. physiol. Chem., **11**, 184 (1887).

Görte, Dissertation, Erlangen, 1902.

Nothnagel, Arch. Phar., **232**, 261 (1894).

Schmidt, Arch. Phar., **229**, 467 (1891).

Herberger, Berzelius' Jahresb., **12**, 273 (1833). "Fagin" = choline.

Thoms, Ber. chem. Ges., **31**, 271 (1898).

Schulze and Frankfurt, Ber. chem. Ges., **26**, 2151 (1893).

Schulze, Frankfurt and Winterstein, Landw. Vers.-Stat., **46**, 383 (1895).

Kunz, Arch. Phar., **225**, 461 (1887); **223**, 721 (1886); **226**, 529 (1888).

Struve, Zeit. anal. Chem., **41**, 544 (1903).

Kunz-Krause, Arch. Phar., **231**, 613 (1893); **237**, 1 (1899).

Wenzell, Jahresb. Chem., 1864, 14.

Boehm and Külz, Arch. exp. Path., **19**, 403 (1865).

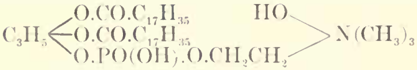
Boehm, Arch. Phar., **222**, 159 (1884).

Hoppe-Seyler, Zeit. physiol. Chem., **2**, 427 (1879); **3**, 374 (1879).

Loew, Arch. gesammt. Physiol., **19**, 342 (1879).

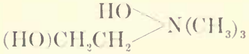
Struve[b] has further distinguished between lecithin and water-soluble choline compounds and water-insoluble choline proteid bodies, the existence of which in plants has not yet been demonstrated.

The lecithins are closely related to the fats in constitution and are found in all vegetable tissues, being fully as widely distributed as the proteids and sugars, in all possible organs, and in every cell. According to Aso[c] small quantities of lecithin are present in soils rich in organic matter. The lecithin molecule contains the grouping of palmitic, stearic, or oleic acid, and the grouping of choline. The constitution of stearin lecithin may be represented by the following formula:



$$C_3H_5\left\langle\begin{array}{l}O.CO.C_{17}H_{35} \qquad\qquad HO\\ O.CO.C_{17}H_{35}\\ O.PO(OH).O.CH_2CH_2\end{array}\right\rangle N(CH_3)_3$$

and that of choline thus:



$$\left.\begin{array}{r}HO\\ (HO)CH_2CH_2\end{array}\right> N(CH_3)_3$$

Choline can be prepared synthetically[d] and is a sirupy liquid or highly hygroscopic crystalline mass of alkaline reaction. By boiling in aqueous solution it is decomposed into glycol and trimethylamine.

The lecithins are readily decomposed and split off choline and complex glycerophosphoric acids, which by further decomposition yield fatty acids, glycerin, and phosphoric acid. It is such a decomposition which takes place in germinating seeds and also in seedlings in the absence of light. During the process of germination comparatively large quantities of phosphoric acid are found in the water in which the seeds are lying, and this again disappears as the seedling begins to grow. This fact has repeatedly been demonstrated with germinating wheat in this laboratory, and the exudation of phosphoric acid by a large number of germinating seeds has also been shown by other investigators.

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[a] See especially Schulze, Zeit. physiol. Chem., **15**, 140 (1891), in this connection.

[b] Ann. Chem., **330**, 374 (1903).

[c] Bul. Coll. Agr., Tokyo, **6**, 277 (1904).

[d] Wurtz, Compt. rend., **65**, 1015 (1868).

Schmidt and Bode, Arch. Phar., **229**, 469 (1891); Ann. Chem., **267**, 268, 300 (1891).

Kruger and Bergell, Ber. chem. Ges., **36**, 2901 (1903).

This liberation of phosphoric acid by germinating seeds is the direct result of such decomposition of the lecithins as described above. According to Zalewski,[a] this decomposition of the lecithins is due to an enzyme. He has further shown that organic phosphorus compounds are quickly and almost totally decomposed by this enzyme during the process of germination, only 2 per cent remaining unattacked. The decomposition of lecithin by bacteria, with the formation of choline, has also been studied by Ruata and Caneva,[b] and observations of choline in the presence of certain bacteria were also made by Schmidt.[c]

Choline is formed as a product of this decomposition of the lecithins, and its wide distribution in the vegetable kingdom is therefore not at all surprising, and under certain circumstances the quantity liberated in this process may be, comparatively speaking, large.

The effect of choline on seedling wheat plants was therefore tried. The choline was obtained in a pure form (Merck's) and when introduced in varying amounts into water cultures of wheat it showed itself to be mildly toxic to wheat seedlings. The plants grown in this solution are shown in Plate I, fig. 2. In the lower concentrations, from 1 to 100 parts per million, the seedlings, more especially the roots, were stimulated to increased growth, behaving in this respect like other minute amounts of toxic materials and similar to the effect displayed when a toxic soil is treated with an absorbing agent or sometimes when merely diluted with water, as shown in a previous bulletin. Concentrations above 100 parts per million were distinctly toxic, producing a retardation in root and top development, although even a concentration of 1,000 parts per million was not fatal to the plants.

The almost universal distribution of choline directly in plant tissues and as the degradation product of the lecithins makes its presence in soils in which plants are growing and decaying highly probable, at least as an intermediary product of the changes which take place in the plant remains in the soil, and this has a still greater significance when we consider the closely related body neurine.[d] Neurine ($C_5H_{13}NO$) is in all probability formed from choline or its mother sub-

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[a] Ber. bot. Ges., **24**, 285 (1906).

[b] Ann. d'igiene sperim., **11**, 341 (1901).

[c] Arch. Phar., **229**, 467 (1891).

[d] Hofmann, Compt. rend., **47**, 558 (1858).
Liebreich, Ber. chem. Ges., **2**, 12 (1869).
Brieger, Ber. chem. Ges., **16**, 1186, 1405 (1883); **17**, 516, 1137 (1884).
Marino-Zucco, Ber. chem. Ges., **17**, 1043 (1884).
Hundeshagen, Jour. prakt. Chem., **136**, 245 (1883).
Gulewitsch, Zeit. physiol. Chem., **26**, 175 (1898).

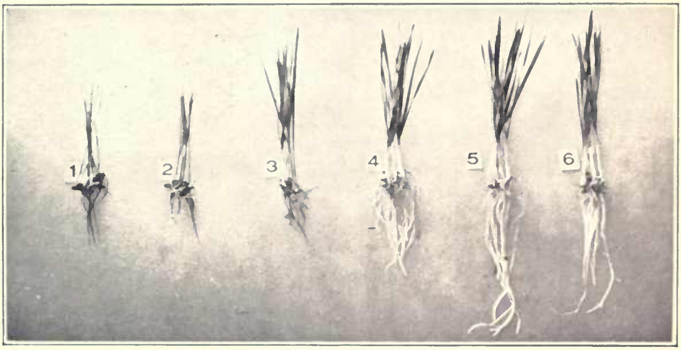


FIG. 1.—EFFECT OF PIPERIDINE, FOUND IN PEPPER PLANTS AND OCCURRING IN MANY VEGETABLE POISONS LIKE ALKALOIDS.

[Wheat grown in: (1) Solution of piperidine, 500 parts per million; (2) 250 parts; (3) 100 parts; (4) 25 parts; (5) 1 part; (6) control in pure distilled water.]

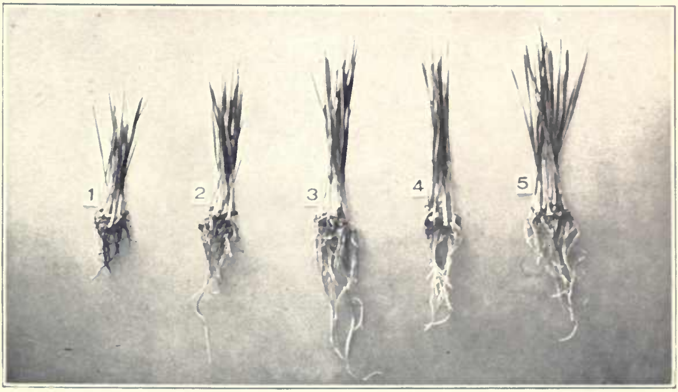


FIG. 2.—EFFECT OF QUINONE, FOUND TO RESULT FROM THE ACTION OF A SOIL FUNGUS ON PROTEIDS.

[Wheat grown in: (1) Solution of quinone, 50 parts per million; (2) 25 parts; (3) 10 parts; (4) 1 part; (5) control in pure distilled water.]

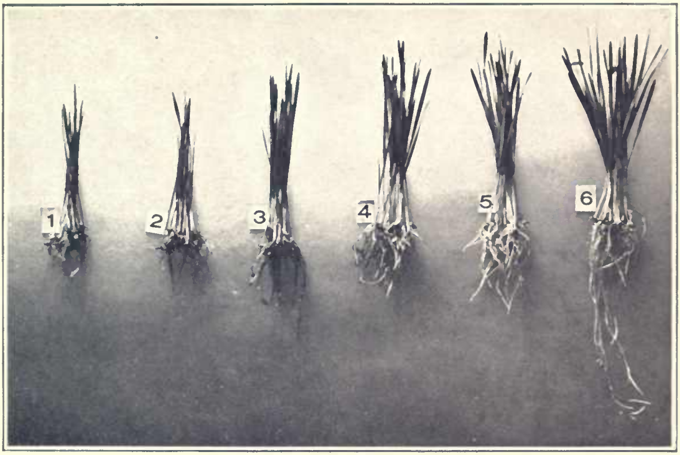


FIG. 1.—EFFECT OF VANILLIN, FOUND IN VANILLA BEANS, LUPINES, BEETS, ROOTS, OATS, DECAYED WOOD, ETC.

[Wheat grown in: (1) Solution of Vanillin, 1,000 parts per million; (2) 500 parts; (3) 100 parts; (4) 25 parts; (5) 1 part; (6) control in pure distilled water.]

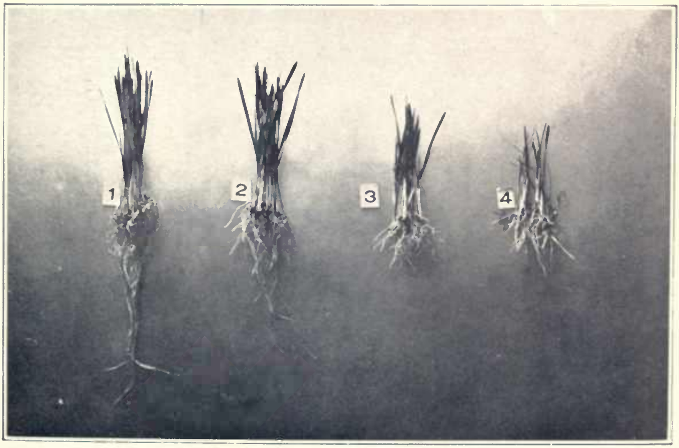
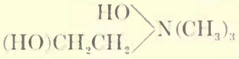


FIG. 2.—EFFECT OF CUMARIN, OCCURRING IN TONKA BEANS, SWEET SCENTED GRASSES, SWEET CLOVER, ETC., AND FORMED BY THE ACTION OF MOLD FUNGI ON CARBOHYDRATES.

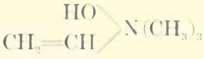
[Wheat grown in: (1) Control in pure distilled water; (2) solution of cumarin, 1 part per million; (3) 25 parts; (4) 50 parts.]

stance, lecithin, by the life processes of certain microorganisms,[a] but has not yet been found in plants as such. By the action of dilute sulphuric acid lecithin is slowly decomposed, the choline under these circumstances being also readily changed to neurine. Neurine and choline can, moreover, be changed from one to the other by artificial processes. The close relationship of these two compounds is shown by the following formulas:



$$\left.\begin{matrix}HO\\(HO)CH_2CH_2\end{matrix}\right\rangle N(CH_3)_3$$

Choline



$$\left.\begin{matrix}HO\\CH_2{=}CH\end{matrix}\right\rangle N(CH_3)_3$$

Neurine.

The neurine differs from choline by having one molecule of water less in its composition. Neurine belonging to the class of bodies known as ptomaines or toxines is very poisonous when introduced into the animal organism, and it was also found to be far more toxic to wheat seedlings in water cultures than was the choline.

A sample of neurine, prepared by Merck, was tested in water cultures with wheat seedlings in the same manner as choline. The lowest concentrations (6 parts per million) stimulated the growth, thus being analogous to the action of choline and toxic substances generally in low concentrations, but the plants were already greatly injured in a solution containing 25 parts per million, and a solution of 250 parts per million killed the seedlings in a few days. When the neurine was neutralized with acetic acid the same effects were obtained. It is thus evident that the neurine is very much more toxic than corresponding quantities of the higher oxygenated choline, which can even serve as a source of carbon for microorganisms. This toxicity of neurine to plants, in view of the fact that it can be formed under certain conditions by the action of microorganisms on the widely distributed choline and lecithin of plant remains, as well as by quite simple chemical reactions from choline, has considerable interest in connection with toxic soil conditions and the improvement following nitrification in such soils. The process of nitrification consists in the intermediary formation of nitrous acid. Neurine, as is readily seen from the formula, contains the vinyl group having a double linking of carbon atoms. Compounds of this nature readily add nitrous acid, forming very unstable and highly reactive nitroso derivatives which undergo further changes. It is possible, therefore, that if a body like neurine existed in a soil the nascent formation of nitrous acid might bring about a deep-seated change, rendering the toxic material harmless.

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[a] Schmidt and Weiss, Arch. Phar., **229**, 481 (1891).

Betaine or oxyneurine ($C_5H_{11}NO_2$),[a] which is closely related to both choline and neurine, is also found widely distributed in seeds and plants and can be derived artificially from choline by oxidation, with loss of water. In contrast with the toxic neurine, this oxyneurine was distinctly beneficial to the seedlings which grew well in concentrations ranging from 1,000 to 5 parts per million. It is classed by Loew[b] among the compounds serving as a good source of carbon for bacteria and lower forms of plant life. It will be noted that this behavior of neurine, choline, and betaine toward wheat is in harmony with the results noted previously in this bulletin in the case of tyrosine or homogentisinic acid, namely, that the oxidized form of a toxic substance may be entirely harmless or even beneficial.

OTHER NITROGENOUS BODIES.

Urea derivatives.—Alloxan ($C_4H_2N_2O_4$), the ureïde of mesoxalic acid, has not been reported as occurring in plants, although alloxantin, a product of the reduction of alloxan,[c] has been prepared from convicine. This convicine is obtained from the seeds of *Vicia faba* and *V. sativa* and from beet juice.[d]

Alloxan is stated by Loew[e] to be an unfavorable source of carbon for bacteria. At the end of ten days the wheat plants which had grown in the solution of alloxan containing 1,000 parts per million were dead, those in 100 parts per million were injured, while those in concentrations of 25, 5, and 1 parts per million were somewhat stimulated. Alloxan thus exhibits all the properties of a toxic substance in its action upon the growth of plants.

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[a] Ritthausen and Weger, Jour. prakt. Chem., **138**, 32 (1884).
Maxwell, Am. Chem. Jour., **13**, 469 (1891).
Scheibler, Zeit. Chem., 1866, 279; Ber. chem. Ges., **2**, 292 (1869); Ber. chem. Ges., **3**, 155 (1870).
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v. Planta, Ber. chem. Ges., **23**, 1699 (1890).
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Griess, Ber. chem. Ges., 8, 1406 (1875).
Marme and Husemann, Ann. Chem. Suppl., **2**, 383 (1863).
Marme and Husemann, Ann. Chem. Suppl., **3**, 245 (1864); Arch. Phar., **207**, 289 (1875).
Kraut, Ann. Chem., **182**, 180 (1876).
Schulze, Ber. chem. Ges., **22**, 1827 (1889); Zeit. physiol. Chem., **17**, 193 (1893).
Schmidt and Schütte, Arch. Phar., **229**, 523 (1891).

[b] Loew, Bul. Coll. Agr., Tokyo, **2**. 51 (1894).

[c] Ritthausen, Jour. prakt. Chem., **132**, 218 (1881); **167**, 487 (1899); **137**, 259 (1884); Ber. chem. Ges., **29**, 894, 2106 (1896).

[d] von Lippmann, Ber. chem. Ges., **29**, 2653 (1896).

[e] Loew, Chem. Energie d. lebenden Zellen. München, 1899, 69.

Guanine ($C_5H_5N_5O$), which is a constituent of guano, has also been found to be a product of the autolysis of yeast.[a] It appears to be rather widely distributed and has been found in the seeds of vetch, alfalfa, clover, and gourd,[b] in germinating barley,[c] in sugar beet,[d] and in sugar cane.[e] Guanine is so slightly soluble in water that it was not possible to test its action in solutions having a concentration greater than 40 parts per million. Its effect upon wheat plants was tried in concentrations of 40, 20, 10, 5, and 1 part per million. In all these concentrations the guanine had a slightly beneficial effect upon the growth of the plants.

Xanthine ($C_5H_4N_4O_2$), which is closely related to guanine, has been reported as occurring in a number of plants.[f]

Xanthine is so difficultly soluble in water that it was only tested in concentrations of 25, 10, 5, and 1 part per million. In all of these concentrations it exerted a slightly beneficial effect.

Guanidine (CH_5N_3) has been demonstrated in plants by Schulze[g] and von Lippman,[h] and according to the investigations of Kutscher[i] guanidine may arise from the oxidation of arginine which is another proteid decomposition product found in plants. Interesting in this connection is the appearance of guanidine in seedlings, reported by Schulze, which probably results by further changes from arginine. Guanidine may be formed artificially by the oxidation of guanine. Guanidine was first shown to be toxic to plants by Kawakita,[j] who found that a concentration of 2,000 parts per million guanidine hydrochloride was sufficient to kill young barley plants in three days.

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[a] Schutzenberger, Ber. chem. Ges., **1**, 192 (1869).

[b] Schulze, Zeit. physiol. Chem., **9**, 420 (1885); **10**, 80, 326 (1886); Jour. prakt. Chem. (2), **32**, 433 (1885).

[c] Ullik, Chem. Centr., 1887, 829.

[d] von Lippmann, Ber. chem. Ges., **29**, 2645 (1896).

[e] Shorey, Jour. Am. Chem. Soc., **21**, 609 (1899).

[f] Salomon, Dubois' Arch., 1881, 161, 361; Bot. Jahresber. 1880 (1), 290.
Schulze, E., Landw. Jahrb., **12**, 909 (1883); Jour. prakt. Chem., **35**, 337 (1883); Landw. Vers.-Stat., **46**, 383 (1895).
Schulze and Steiger, Zeit. physiol. Chem., **9**, 43 (1887).
Menozzi, Ber. chem. Ges., **21**, 619 (1888).
Baginsky, Zeit. physiol. Chem., **8**, 395 (1884).
von Lippmann, Ber. chem. Ges., **29**, 2645 (1896).

[g] Zeit. physiol. Chem., **17**, 197 (1892).

[h] Ber. chem. Ges., **29**, 2645 (1896).

[i] Zeit. physiol. Chem., **32**, 413 (1897).

[j] Bul. Coll. Agr., Tokyo, **6**, 182 (1904).

He also found that while fungi were able to utilize guanidine hydrochloride as a source of nitrogen they were unable to use it as a source of carbon.

Guanidine carbonate in distilled water was tested on wheat plants in concentrations of 1,000 parts per million and less. The plants were killed in solutions of 100 parts per million and stronger in nine days. In all the lower concentrations, including 1 part per million, the wheat plants were seriously injured.

Skatol (C_9H_9N) is a common product of putrefaction of proteid materials and is known to be the product of the activities of certain bacteria. In solutions skatol proved to be somewhat toxic to wheat plants. A concentration of 200 parts per million was sufficient to kill seedling plants in nine days, and in the same time a concentration of 50 parts per million was injurious. In those concentrations where skatol had a harmful effect the roots of the wheat plants were more injured than the tops.

Pyridine (C_5H_5N) forms the nucleus upon which are built many of the alkaloids. It is obtained chiefly from coal tar, but may also be obtained from a number of alkaloids, such as nicotine, trigonelline, sparteine, and cinchonine, when these are highly heated, treated with alkalies, or distilled with zinc dust. Pyridine is a colorless liquid of penetrating odor and basic properties.

The action of pyridine and its homologues has received added importance for agriculture as a result of the investigations of Shorey,[a] who obtained pyridine by the dry distillation of soil. The author cited says (p. 37): "As the fat in this soil was found to be only 0.005 per cent, it does not seem likely that the pyridine formed was due to the formation of the pyridine ring by condensation, but rather that it exists already in some form in the soil." Pyridine was also obtained from the same soil after extraction with ether; hence it seems that the view taken is the correct one. The presence of pyridine-like substances in soils was suggested by Berthelot and André,[b] who attempted to isolate the compounds which give the characteristic odor to soils.

Laurent[c] found that a 1 per cent solution of pyridine was toxic to the fungi which he studied. It has been observed by Falkenburg[d] that the vapor of pyridine and some of its homologues is poisonous to bacteria.

In the experiments with wheat seedlings it was found that pyridine although not sufficiently toxic at a concentration of 1,000 parts per million to kill wheat plants in nine days, was nevertheless very injurious, especially to the growth of the green parts of the plants. In a concentration as low as 50 parts per million the growth of the tops was inhibited and the leaf tips turned brown. In the lower concentrations there was no stimulation of growth.

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[a] Shorey, Rept. on Agr. Investigations in Hawaii, 1905; Bul. 170, Off. Expt. Sta., U. S. Dept. Agr., 1906.

[b] Berthelot et André, Compt. rend., **112**, 598 (1891).

[c] Laurent, Ann. Soc. Belge Micr., **14**, 29 (1890).

[d] Czapek, Biochemie der Pflanzen, II, 926.

Picoline ($C_5H_4N.CH_3$), or methyl pyridine, was toxic to wheat plants, but only killed in the concentrations of 1,000 parts per million, and did not cause injury below 500 parts per million. The injury seemed to be manifested by the tops more than by the roots, thus resembling the action of pyridine.

Piperidine ($C_5H_{11}N$), or hexahydropyridine, is known to occur in nature, for example, in the pepper plant, and forms the nucleus of many alkaloids. Solutions of piperidine killed and injured at a lower concentration than either pyridine or picoline. A sample of piperidine that was neutralized with acetic acid proved to be more toxic than the strongly alkaline piperidine itself. Piperidine seems to injure the roots more severely than the tops.

Quinoline (C_9H_7N) forms the nucleus of many alkaloids found in plants belonging to the families Rubiaceæ and Loganiaceæ. Falkenburg[a] found that quinoline was toxic to bacteria in a concentration of 2,000 parts per million. Reference to Table I shows that quinoline was sufficiently toxic to kill wheat plants at a concentration of 500 parts per million. So low a concentration as 5 parts per million affected them injuriously in six days. None of the lower concentrations caused stimulation of growth.

Ricin is the poisonous (for animals) principle of the castor oil plant (*Ricinus communis*). Its chemical composition is unknown, but it probably is a toxalbumen. Bokorny[b] found that ricin was very slightly toxic to algæ and infusoria. On account of its insolubility no tests could be made upon solutions having a concentration greater than 50 parts per million. The wheat plants were injured to a slight extent in solutions below 30 parts per million, but most of the injury found was in solutions containing 40 and 50 parts per million. The roots always showed greater injury than the tops.

Mucin has been isolated from various animal tissues, and in one instance from plants, viz, the yams, *Dioscorea japonica* and *D. batatas*.[c] Mucin is comparatively insoluble in water, and hence a wide range of concentrations was not available for testing its properties upon plants. In a saturated solution there was practically no growth of the roots of the wheat plants. In a solution of 100 parts per million, which is somewhat below the point of saturation, the plants were seriously injured, both in the growth of roots and of tops. At a concentration of 5 parts per million mucin had a stimulating effect upon the growth of wheat plants. Both roots and tops were better than those of plants grown in distilled water.

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[a] Czapek, Biochemie der Pflanzen, II, 926.

[b] Bokorny, Th., Arch. gesammt. Physiol., **64**, 262 (1896).

[c] Ishii, Landw. Vers.-Stat., **45**, 434 (1894); Beihefte Bot. Centr., **6**, 20 (1896); Bul Coll. Agr., Tokyo, **2**, 97 (1894).

NONNITROGENOUS BODIES.

Pyrocatechin ($C_6H_4(OH)_2$), or *o*-dioxybenzene, has been found in the sap of *Mimosa catechu*, in the green leaves and berries of *Ampelopsis quinquefolia*,[a] in the sap of sugar beets,[b] and in several species of willow.[c] The characteristic black color which the leaves of certain species of willows assume upon drying is probably the result of the oxidation of the pyrocatechin through the activity of an oxidase. Pyrocatechin may be formed as a decomposition product from many aromatic vegetable compounds, and even from sugar. It was shown by Yabe to be fatal to yeast cells and bacteria when used in concentrations of 0.4 to 0.58 per cent.[d]

The effect of pyrocatechin was harmful, though not as toxic as some substances tried. Like many other toxic agents it was stimulating at low concentrations. The solution of 1 part per million gave slightly better plants than the control in distilled water.

Arbutin ($C_{12}H_{16}O_7$), which is a glucoside of hydroquinone (paradioxybenzene) is widely distributed among plants, especially in the Ericaceæ, or heath family. Klebs[e] found that a 0.5 per cent solution of arbutin inhibited zoospore formation in *Conferva minor*. In its effect upon wheat plants arbutin is quite similar to pyrocatechin. It causes injury at about the same concentration and exerts a stimulating effect in the lower concentrations.

Pyrogallol ($C_6H_3(OH)_3$) has been more or less extensively tried on wheat seedlings and its effects described in experiments reported in Bulletins 28, 36, and 40 of this Bureau. In solutions of greater concentration than 25 parts per million it is usually toxic to wheat plants, but is stimulating in low concentrations. It was oxidized by the roots of the plants growing in it.

Phloroglucin ($C_6H_3(OH)_3$), like pyrogallol, is not found as such in plants, but may be derived from several aromatic plant constituents. Its toxic properties have been described by Bovert.[f] Reference to Table I shows that its toxic properties are quite similar to those of pyrogallol. In common with pyrogallol this substance was oxidized by the roots of the seedling plants which grew in it.

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[a] v. Gorup Besanez, Ber. chem. Ges., **4**, 905 (1871); Sitzungsb. med.-phys. Soc. Erlangen, **5**, 39 (1873).

[b] Lippmann, Ber. chem. Ges., **20**, 3298 (1887).

[c] Weevers, Jahrb. wiss. Bot., **39**, 229 (1903).

[d] Yabe, Bul. Coll. Agr., Tokyo, **2**, 73 (1894).

[e] Die Bedingungen der Fortpflanzung bei einigen Algen u. Pilzen. Jena, 1896.

[f] Jour. prakt. Chem., **127**, 445 (1878); Ber. chem. Ges., **12**, 2012 (1879).

Vanillin ($C_8H_8O_3$), the aromatic principle of the vanilla bean, is methyl protocatechuic aldehyde. It is probably not found as such in living plants, but exists in the form of a glucoside, which breaks down into vanillin and a sugar when the plant organs are dried. The glucoside, which gives rise to vanillin, probably occurs in a large number of plants. Vanillin, or substances which give rise to it, has been reported in oats (seeds and roots),[a] seeds of the white lupine,[b] asparagus shoots,[c] in raw beet sugar,[d] in Ilex leaves,[e] in dahlia roots,[f] etc. According to von Lippmann vanillin seems to arise during the decay of wood under certain conditions.[g]

Behrens[h] reported that when the odorless sap of fresh vanilla leaves was boiled with dilute sulphuric acid a perceptible vanilla odor was detected. Busse[i] has shown that the characteristic vanilla odor is obtained when the sap of the fruits of the vanilla bean (*Vanilla pompona*) is acted upon by emulsin. This would indicate that the plants contained a vanillin glucoside.

Vanillin solutions were shown by Klebs[j] to be fatal to the alga, *Conferva minor*.

The solutions of vanillin were distinctly toxic to wheat seedlings in our experiments, 500 parts per million being sufficient to kill wheat plants in nine days. In all the stronger concentrations the roots were quickly killed and became slimy. Before death ensued the roots were able to oxidize part of the vanillin to a purple insoluble dye which was deposited upon the surface of the roots. Reference to Plate III, figure 1, will show that the roots of plants grown in concentrations greater than 100 parts per million are dyed a dark color as a result of the oxidation of the vanillin. The toxic effects of the vanillin were less marked upon the tops of the wheat plants than upon their roots, nevertheless the green weight of the tops in all solutions was less than that of the tops of control plants grown in distilled water. The green weight of tops of plants grown in a vanillin solution so dilute as 1 part per million was 91 per cent of the controls and their transpiration was 72 per cent of the controls.

In some later experiments a few instances were found in which vanillin exerted a stimulating effect upon root growth when used in the lower concentrations. This may perhaps be regarded as a phenomenon commonly exhibited by the oxybenzenes and their derivatives.

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[a] de Rawton, Compt. rend., **125**, 797 (1897).

[b] Campani and Grimaldi, Chem. Centr., 1888, I, 377.

[c] von Lippmann, Ber. chem. Ges., **18**, 3335 (1885).

[d] Scheibler, Ber. chem. Ges., **13**, 335 (1880); Lippmann, ibid., 662.

[e] Polenske and Busse, Arb. kais. Gesundheitsamt. **15**, 171 (1899).

[f] Payen, Ann. chim., **24**, 209 (1823); von Lippmann, Ber. chem. Ges., **39**, 4147 (1906).

[g] von Lippmann, Ber. chem. Ges., **37**, 4521 (1904).

[h] Tropenpflanzen, **3**, 299 (1899).

[i] Zeit. Untersuch. Nahr. u. Genuss., **3**, 21 (1900).

[j] Die Bedingungen der Fortpflanzung bei einigen Algen u. Pilzen. Jena, 1896.

Vanillic acid ($C_8H_8O_4$), a monomethyl-protocatechuic acid, may be formed by the energetic oxidation of the aldehyde vanillin, or of coniferin. The solutions of vanillic acid showed marked toxic properties toward wheat plants. As in the case of vanillin, the oxidizing power of the roots formed, in the higher concentrations, an insoluble purple-brown dye which was deposited upon the surface of the roots. (Plate V, fig. 2.) Wheat plants were killed in seven days in the solutions containing 100 parts per million of vanillic acid. At a concentration of 25 parts per million only the roots of the plants were poorer than the control plants. In concentrations of 5 parts per million and 1 part per million the roots and tops were all better than those of the control plants. It thus appears that the vanillic acid is less inhibitive of root growth than the aldehyde, vanillin; in this respect it resembles more closely the action of the oxybenzenes than does vanillin.

Quinic acid ($C_6H_7(OH)_4.COOH$) is found in cinchona bark, always accompanying the alkaloid, quinine. It is also found in other rather distantly related plants; in beet leaves,[a] in moor hay,[b] in cranberry leaves,[b] and in other plants.[c]

By the action of mold fungi quinic acid is broken up into proprionic acid, acetic acid, and formic acid.

In all except the more dilute solutions quinic acid was very toxic to wheat plants. At the end of ten days the entire plants in concentrations of 1,000 and 500 parts per million were dead; in 100 parts per million only the roots were dead. In concentrations below 50 parts per million the plants were as good as the controls grown in distilled water, and in the solutions containing 5 parts per million there was slight stimulation of growth.

Quinone, $C_6H_4O_2$, benzoquinone, may be prepared artificially from quinic acid or from hydroquinone. It is a compound of interest in the study of soil problems since Beijerinck[d] has found that a soil fungus, *Streptothrix chromogena*, has the ability to form quinone from proteids.

Quinone has been shown to be toxic to yeast by Laurent[e] and to the seedlings of various plants, algæ, and fungi by Furuta.[f] The last named investigator found that in concentrations of 1,000 and

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[a] von Lippmann, Ber. chem. Ges., **34**, 1159 (1901).

[b] Loew, O., Jour. prakt. Chem., **19**, 309 (1878); **20**, 476 (1879).

[c] Huseman-Hilger, Pflanzenstoffe, **2**, p. 1399.

[d] Beijerinck, Centralbl. f. Bakt., Abt. 2, **6**, 2 (1900).
Arch. Neerland. d. Sc. exactes et nat. (3), **3**, 327 (1900).

[e] Laurent, Ann. Soc. belge. Micr., **14**, 29 (1890).

[f] Furuta, Bul. Coll. Agr., Tokyo, **4**, 407 (1902).

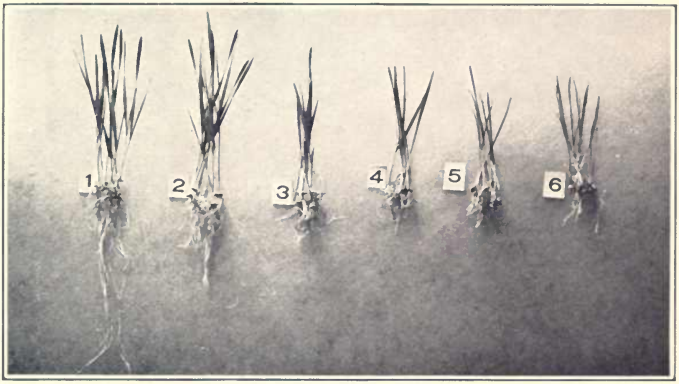

FIG. 1.—EFFECT OF CINNAMIC ACID, FOUND IN CERTAIN PLANTS AND RELATED TO CUMARIN.

[Wheat grown in: (1) Control in pure distilled water; (2) solution of cinnamic acid, 1 part per million; (3) 25 parts; (4) 50 parts; (5) 100 parts; (6) 350 parts.]

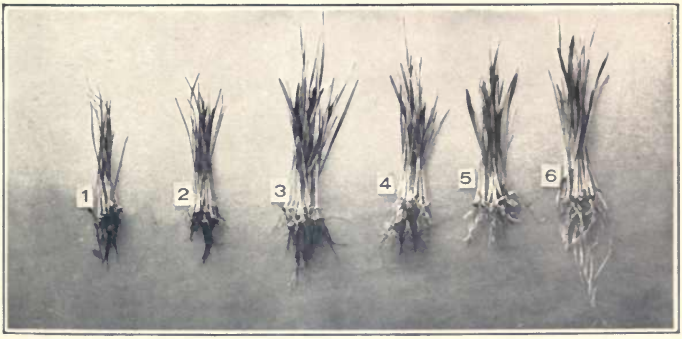

FIG. 2.—EFFECT OF ESCULIN, CLOSELY RELATED TO CUMARIN AND FOUND IN VARIOUS PLANTS.

[Wheat grown in: (1) Solution of esculin, 1,000 parts per million; (2) 500 parts; (3) 100 parts; (4) 25 parts; (5) 1 part; (6) control in pure distilled water.]

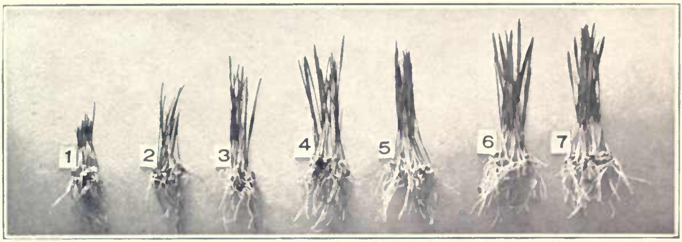

FIG. 1.—EFFECT OF HELIOTROPINE.

[Wheat grown in: (1) Solution of heliotropine, 1,000 parts per million; (2) 500 parts; (3) 100 parts; (4) 25 parts; (5) 10 parts; (6) 1 part; (7) control in pure distilled water.]

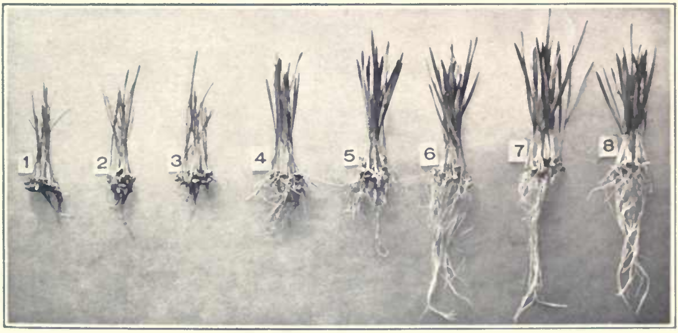

FIG. 2.—EFFECT OF VANILLIC ACID.

[Wheat grown in: (1) Solution of vanillic acid, 500 parts per million; (2) 250 parts; (3) 100 parts; (4) 50 parts; (5) 25 parts; (6) 5 parts; (7) 1 part; (8) control in pure distilled water.]

500 parts per million the roots of soy bean and wheat seedlings were injured within a few hours and killed in three or four days. Filaments of algæ were killed in a concentration of 1,000 parts per million in three or four hours and fungi in a somewhat longer period.

By reference to Table I (see p. 38) it will be seen that quinone was one of the most active poisons employed in the series of experiments. Wheat plants were entirely killed in solutions containing 100 parts per million and seriously injured in solutions containing 50 parts per million. In the lower concentrations, including 1 part per million, there was a slight inhibition of growth. No stimulation of growth was noticed in any of the concentrations tried.

Cinnamic acid is a phenol acid which is present in the bark of certain plants and forms esters which are found in the leaves of various other plants. Its effects upon the growth of seedlings was studied on account of its relation to cumarin. Cinnamic acid was found by True,[a] to be fatal to the root tips of *Lupinus albus* in twenty-four hours when employed in a concentration of $\frac{m}{12800}$ (12 parts per million). The same investigator also found that sodium cinnamate was toxic to root tips when employed in a concentration of $\frac{m}{800}$ (184 parts per million). Using a slightly different method and different plants, the results obtained with wheat seedlings varied, naturally, from those obtained with lupine. The same relations, however, hold true in both cases. Cinnamic acid is strongly toxic for seedlings, and its sodium salt is moderately toxic. Cinnamic acid is particularly toxic to the growth of roots. Reference to Plate IV, figure 1, shows that in all concentrations the growth of roots was inhibited. In fact it was only in concentrations weaker than 25 parts per million that there was any elongation of roots.

Cumarin ($C_9H_6O_2$) is a lactone of orthocumaric acid which may be regarded as oxy-cinnamic acid. Cumarin is a substance which has been found in a number of plants in different families of the plant kingdom. Among others, cumarin has been reported in the following plants: In grasses, viz, Anthoxanthum (Sweet Vernal), Hierochloë (holy grass), Milium, Cinna,[b] in various dicotyledons, viz, Herniaria, Ruta (common beet), *Prunus mahaleb*, Dipterix, Melilotus (sweet clover), Toluifera, *Alyxia stellata*,[c] the tubers of *Vitis sessi-*

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[a] Am. Jour. Sci. (4), **9**, 182 (1900).

[b] Poulsen, Bot. Centr., **15**, 415 (1883).

[c] Proc. Amer. Phar. Assoc. **36**, 581, (1888).

flora,[a] *Galium triflorum* (bedstraw),[b] *Asperula odorata* (woodruff), *Ageratum mexicanum,*[c] and *Liatris odoratissima.*[d]

Ortho-cumaric acid and o-hydrocumaric acid (Melilotic acid) are found in Melilotus, the sweet clover,[e] in addition to cumarin.

Para-hydrocumaric acid, although it has not been reported in plants, is of interest on account of its relation to tyrosine. Through the action of bacteria, the amide group in tyrosine is broken up and ammonia liberated, thus giving rise to p-hydrocumaric acid. It is also of interest to note that Gosio[f] has found that cumarin may be formed from carbohydrates by the action of certain mold fungi, e.g. *Aspergillus glaucus, A. varians, A. novus,* and *A. flavescens.*

Solutions of cumarin were shown to be toxic to the alga *Conferva minor* by Klebs,[g] when used in strong concentrations.

The experiment showed that cumarin is extremely poisonous to wheat plants. At the end of five days the plants in 250 parts per million and stronger were dying, the roots and tops having made practically no growth. The root tips were swollen and slightly discolored, although the roots themselves were quite turgid. When the experiment was discontinued at the end of eight days the plants in the solutions of 100 parts per million were dead, although they had made a slight growth at the beginning of the experiment. The roots were discolored for a distance of 3 to 6 mm. from the tip and their surface was very slimy, due to the death of the outer layers of cells, which were then beginning to peel off. The leaves of the affected plants were short and broad, a feature not brought out by the illustrations, but which was very characteristic in all experiments with cumarin. The cumarin appeared to injure the meristematic tissue of the stem in such a way that only the first leaves were unfolded, and in most cases the sheathing leaf base was more or less swollen by the abnormal growth of the inhibited leaves within it.

The plants in the solutions of 50 parts per million were alive at the end of eight days, but all growth had ceased. The root tips were discolored and badly swollen. The leaves were dead for a considerable distance back from the tips. In the solution of 1 part per million the development of tops, as shown by the illustration (Plate III, Fig. 2), was practically equal to that of the control plants in distilled water. The root development was not as good, however, the tips being slightly discolored but not swollen.

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[a] Peckholt, Zeit. Allg. österr. Apothek.-Ver., 1893, 829.

[b] v. Cotzhausen, Am. Jour. Phar., **48**, 405 (1876).

[c] Molisch and Zeisel, Ber. bot. Ges., **6**, 353 (1888).

[d] Vide Just's Bot. Jahresb., 1874, II, 947.

[e] Zwenger and Bodenbender, Ann. Chem., **126**, 257 (1863).

[f] Atti R. Accad. Lincei, Classe sci. fis. mat. nat. (V) **15** (2) 59, (1906); abstr. Jour. Chem. Soc., **90**, 699, (1906).

[g] Die Bedingungen der Fortpflanzung bei einigen Algen u. Pilzen. Jena, 1896.

Daphnetin ($C_9H_6O_4$) which occurs in various species of Daphne[a] is a lactone, and is to be regarded as (3, 4) dioxy-cumarin.[b]

Daphnetin was relatively much less toxic than cumarin. On account of its insolubility it was impossible to test daphnetin in concentrations greater than 50 parts per million. At a concentration of 50 parts per million the green weight of tops produced in twelve days was 76 per cent of the controls. In concentrations of 25 parts per million and less the growth of tops was practically as good as in distilled water, and the development of roots was only slightly inferior.

Esculin ($C_{15}H_{16}O_9$) is of particular interest on account of its relation to cumarin. It is the glucoside of esculetin which is a lactone isomeric with daphnetin and shown by Tiemann and Will to be (4, 5) dioxy-cumarin.[c] Both esculin and esculetin have been found in plants, but we know little of how widely distributed they are. Esculin as shown in Table I is decidedly less toxic to plants than cumarin, but more toxic than daphnetin.

A saturated solution of esculin was found by Klebs,[d] to inhibit the formation of zoospores in *Conferva minor*, but it did not prevent the formation of chlamydospores in *Mucor racemosus*. Laurent found that a saturated solution of esculin was not inhibitive to growth of fungi, provided that glycogen were also present.[e]

The esculin solutions had a blue fluorescence, when prepared; this was lost after plants had grown for a time in them. The roots which grew in the stronger solutions were colored dark yellow as a result of their oxidative activities, the dye formed being insoluble and remaining upon the surfaces of the roots where oxidation had occurred. This effect is shown in Plate IV, figure 2. The toxic effects of esculin were more marked upon the roots of the plants than upon the tops. In concentrations of 1,000 and 500 parts per million wheat plants were killed and were injured even in a solution containing 1 part per million. In the solutions containing 100 parts per million there was a distinct stimulation of the growth of tops.

Heliotropine ($C_8H_6O_3$) or piperonal is the aldehyde of piperonylic acid. It possesses the pleasant odor of heliotrope, and is, indeed, found in the flowers of *Nigritella suaveolens*.[f]

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[a] Vauqelin, Ann. Chim., **84**, 173 (1812).
Zwenger, Ann. Chem., **115**, 1 (1860).
Russell, Rev. gen. Bot., **14**, 420 (1902).

[b] Stunkel, Ber. chem. Ges., **12**, 109 (1879).
von Pechmann, Ber. chem. Ges., **17**, 929 (1884).
Gattermann and Kobner, Ber. chem. Ges., **32**, 287 (1899).

[c] Ber. chem. Ges., **15**, 2073 (1882); **15**, 2106 (1883).

[d] Die Bedingungen der Fortpflanzung bei einigen Algen u. Pilzen. Jena, 1896.

[e] Laurent, Ann. Soc. Belge Micr., **14**, 29 (1890).

[f] von Lippmann, Ber. chem. Ges., **27**, 3409 (1894).

The growth of wheat plants in solutions was markedly affected by the presence of heliotropine, although the plants were not killed by a concentration of 1,000 parts per million or less. It is worthy of remark that the tops of the wheat plants were more affected by the heliotropine than the roots. (See Plate V, fig. 1.) The roots were healthy and of nearly equal development in all solutions of heliotropine used.

TERPENE BODIES.

Borneol ($C_{10}H_{18}O$), an alcohol of the terpene series, may be regarded as a secretion of the Borneo camphor tree. From the fact that it is known as a plant secretion, as well as from its relation to camphor, its effects upon wheat plants are of interest. It is noteworthy in this connection that borneol acetate is an important constituent of the aromatic oils of many plants. It occurs, for example, in the needles of different species of pines, firs, spruces, and hemlocks, in golden rod (*Solidago canadensis*), in *Satureja thymbra*, in thyme, etc. The presence of borneol or some of its compounds in soils is not, therefore, unlikely, especially in the vicinity of coniferous trees. Although borneol is markedly insoluble in water, the weak concentrations obtainable were very toxic to both tops and roots of wheat plants. In ten days the plants were killed by a concentration of 100 parts per million and injured by 1 part per million.

Camphor ($C_{10}H_{16}O$), the ketone of borneol, is secreted by different plants, and is notably found in the wood of Cinnamomum, sassafras leaves, cinnamon root, spike, rosemary, basilicum root, etc. The poisonous effects of camphor upon seedlings have long been known. A list of some of the more important works is given below.[a]

The action of camphor on wheat seedlings in our experiments was quite similar to that of borneol. A concentration of 300 parts per million was fatal to the seedlings in eight days, and 5 parts per million produced marked injury.

Terpene containing oils, such as turpentine oil ($C_{10}H_{16}$) are substances to be regarded as excretions of living plants, and many are known to have a toxic effect upon the growth of plants.[a] Heller[b] has made the interesting observation that plants which secrete terpenes are less susceptible to injury by them than are those plants in which terpenes do not occur.

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[a] Treviranus, Physiol. d. Gewächse, **2**, 726.

Conwentz, Bot. Ztg., **32**, 401 (1874).

Heckel, Compt. rend., **80**, 1170 (1875).

Wilhelm, Einwirkung des Camphors auf die Keimkraft (Ref. in Just's Bot. Jahresb., 1876, 884).

Nägeli, Theorie der Gärung, München, 1879, 84-85.

Burgerstein, Landw. Vers.-Stat., **35**, 9 (1888).

Frank, Pflanzenkrankheiten, Breslau, 1895. II Aufl., **1**, 330.

Mesnard, Ann. Sci. Nat. (7), **18**, 257 (1893).

Detto, Flora, **92**, 147 (1903).

Heller, Flora, **93**, 1 (1904).

The action of terpenes has added interest for the study of problems dealing with soil fertility from the fact that the washings from the bark of trees and leaves have been shown[c] to be toxic to seedlings. These washings may contain terpenes or terpenelike bodies, and their retention by the soil in the vicinity of trees would constitute a factor of some importance.

In our experiments turpentine oil proved to be fatal to wheat seedlings in a culture containing 500 parts per million and produced injurious effects at a concentration of 10 parts per million.

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[a] Goldsobel, Just's Bot. Jahresb., 1877, 224.
Nobbe and Hänlein, Landw. Vers.-Stat. **21**, 437 (1878).
Schwartz, Just's Bot. Jahresb., 1881, I, 307.
Omeltschenko, Centr. Bakt., **9**, 813 (1891).
Chamberland, Ann. Inst. Past., **1**, 153 (1887).
Riedlin, Dissertation, München, 1887.
Cadeac and Meunier, Ann. Inst. Past., **3**, 317 (1889).
Bokorny, Arch. gesammt. Physiol., **73**, 555 (1899).
Effront, Compt. rend., **136**, 1556 (1903).

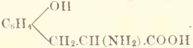
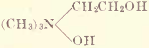
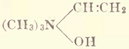
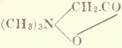
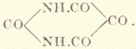
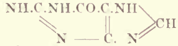
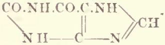
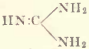
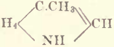
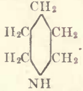
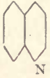
[b] Flora, **93**, 1 (1904).

[c] Bul. 36, Bureau of Soils, U. S. Dept. Agr., 1907.

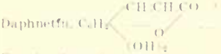
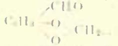
TABULATION OF EXPERIMENTAL RESULTS.

A general summary of the results given in the preceding pages is presented in the following table:

TABLE I.—*Effect of various organic compounds upon the growth of wheat plants, with especial reference to their toxic properties.*

Compound.	Duration of experiment.	Lowest concentration causing death.	Lowest concentration causing injury.	Concentration causing greatest stimulation.	Remarks.
	Days.	*P. p. m.*	*P. p. m.*	*P. p. m.*	
Aspartic acid, $HOOC.CH_2.CH(NH_2).COOH$.	10	500	100	....	Normal growth in concentration below 100 p. p. m.
Asparagine, $NH_2OC.CH_2.CH(NH_2)COOH$.	9	....	....	....	No injury below 1,000 p. p. m.
Glycocoll, $CH_2(NH_2).COOH$	9	....	....	....	Tops of all plants good. Roots slightly injured at higher concentrations.
Alanine, $CH_3.CH(NH_2).COOH$	10	....	500	25	Only roots were injured at 500 p. p. m.
Leucine, $CH_3.(CH_2)_3.CH(NH_2).COOH$	9	....	....	....	No injurious action.
Tyrosine,  $C_6H_4<\begin{matrix}OH\\CH_2.CH(NH_2).COOH\end{matrix}$	11	....	10	....	
Choline,  $(CH_3)_3N<\begin{matrix}CH_2CH_2OH\\OH\end{matrix}$	10	....	500	1	Roots affected more than tops.
Neurine,  $(CH_3)_3N<\begin{matrix}CH{:}CH_2\\OH\end{matrix}$	9	250	25	....	
Neurine (neutralized)	8	250	25	....	
Betaine,  $(CH_3)_3N<\begin{matrix}CH_2.CO\\O\end{matrix}$	9	....	....	....	No injury.
Alloxan,  $CO<\begin{matrix}NH.CO\\NH.CO\end{matrix}>CO$	10	1,000	100	....	
Guanine,  $\begin{matrix}NH.C.NH.CO.C.NH\\N—C.\ N\end{matrix}>CH$	12	....	....	....	Insoluble above 40 p. p. m. No harmful effects.
Xanthine,  $\begin{matrix}CO.NH.CO.C.NH\\NH—C—N\end{matrix}>CH$	10	....	....	....	No injurious action.
Guanidine,  $HN{:}C<\begin{matrix}NH_2\\NH_2\end{matrix}$	9	100	1	....	
Skatol,  $C_6H_4<\begin{matrix}C.CH_3\\NH\end{matrix}>CH$	9	200	50	....	Roots injured more than tops.
Pyridine, C_5H_5N	9	....	50	....	In solutions of 50 p. p. m. and less the root growth was normal.
Picoline, $C_5H_4N.CH_3$	7	1,000	500	100	
Piperidine, 	7	250	25	....	
Piperidine (neutralized)	7	100	25	1	
Quinolin, 	6	500	5	....	
Ricin	10	....	40	....	Insoluble above 50 p. p. m.
Mucin	10	....	100	....	Not tested in concentrations higher than 100 p. p. m.

ABLE I.—*Effect of various organic compounds upon the growth of wheat plants, with especial reference to their toxic properties*—Continued.

Compound.	Duration of experiment.	Lowest concentration causing death.	Lowest concentration causing injury.	Concentration causing greatest stimulation.	Remarks.
	Days.	*P. p. m.*	*P. p. m.*	*P. p. m.*	
rocatechin, $C_6H_4(OH)_2$ 1,2	12	500	25	1	
rbutin, $C_{12}H_{16}O_7$	12	500	25	1	
hloroglucin, $C_6H_3(OH)_3$ 1,3,5	15	500	25	1	
anillin, $C_6H_3\begin{cases}CHO\\O.CH_3\\OH\end{cases}$	9	500	1		
anillic acid, $C_6H_3\begin{cases}COOH\\O.CH_3\\OH\end{cases}$	7	100	25	5	
uinic acid, $C_6H_7(OH)_4COOH$	10	500	100		
uinone, $C_6H_4\begin{cases}O\\O\end{cases}$	9	100	1		
innamic acid, $C_6H_5.CH:CH.COOH$	8	100	25		
odium cinnamate	12		100		Roots were stimulated in lower concentrations.
umarin, $C_6H_4\begin{cases}CH:CH.CO\\O\end{cases}$	8	100	1		
Daphnetin,  $C_6H_2\begin{cases}CH:CH.CO\\O\\(OH)_2\end{cases}$	12		50		Insoluble above 50 p. p. m. Roots somewhat injured.
Esculin, $C_{15}H_{16}O_9$	13	500	1		
Piperonal (heliotropine)  $C_6H_3\begin{cases}CHO\\O\\O\end{cases}CH_2$	7	100	1		
Borneol, $C_{10}H_{17}OH$	10	100	1		
Camphor, $C_{10}H_{16}O$	8	300	5		
Turpentine, $C_{10}H_{16}$	8	500	10		

THE REMOVAL OR AMELIORATION OF TOXIC CONDITIONS.

As a result of the experiments upon the nature and action of the organic bodies studied, it becomes evident that in many respects their similarity to toxic soil conditions is more than casual. It therefore becomes of interest to study the effect of treatments which have been found materially beneficial to toxic soils and their aqueous extracts. Some of these treatments consisted in adding substances which might be regarded as plant nutrients; other treatments which were equally beneficial did not add anything in the nature of a plant nutrient.

THE EFFECT OF TREATMENTS WHICH ADDED NO PLANT NUTRIENTS TO THE SOLUTIONS.

The results of adding absorbing agents and of boiling.—Two of the most toxic substances used in experiments upon plants were guanidine carbonate and neurine. In diminishing their toxicity two treatments, viz, treatment with carbon black and boiling, which have been found remarkably efficient[a] in improving the extracts of toxic soils for the growth of plants, were employed.

The treatment with carbon black consisted in adding a small amount of well-washed carbon black to the guanidine and neurine solution, and shaking them for several minutes. At the end of twenty to thirty minutes the carbon black was filtered out and the solutions used as the basis of water cultures for growing plants. The neurine solution was boiled for a very few minutes in an ordinary flask and, when cool, used for growing plants. The distillate from neurine was prepared by distilling a known quantity of an aqueous solution containing 250 parts per million of neurine. After a portion had passed over the distillate was made up to the original volume of the neurine solution with distilled water and used in water cultures. The effect of these treatments upon the toxic solutions is shown in Table II.

The guanidine carbonate solution was so much improved by treatment with carbon black that a solution which had contained 100 parts per million of guanidine was no more toxic to wheat seedlings than an untreated solution containing 1 part per million. A solution containing 25 parts per million of guanidine after treatment with carbon black gave a better growth of plants than did distilled water.

The neurine solution was so much improved by treatment with carbon black that wheat seedlings grown in a solution which had contained 25 parts per million of neurine made as good growth as the controls grown in distilled water. The plants which grew in a 25 parts per million neurine solution treated with carbon black were even better than those grown in distilled water.

TABLE II.—*Effect of various treatments in altering the critical concentrations of the respective solutions.*

[Parts per million.]

No.	Treatment.	Concentration of the solutions at which the plants were—		
		Killed.	Injured.	Stimulated.
1	Guanidine carbonate	100	1	....
2	Same, treated with carbon black[a]	500	100	25
3	Neurine (neutral)	250	25	....
4	Same, treated with carbon black	250	....	25
5	Same, 250 p. p. m., boiled	Normal growth.		
6	Distillate from neurine solution containing 250 p. p. m	Normal growth.		

[a] The figures in series Nos. 2 and 4 represent the original concentration of solutions which were given the treatments designated, and do not necessarily indicate the concentration of the solution used for growing plants.

The toxic effects of neurine seem therefore to have been entirely removed by boiling or by distilling, as normal growth resulted in those solutions.

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[a] See Buls. 28, 36, and 40 of the Bureau of Soils, U. S. Dept. of Agr.

Without speculating too much upon the nature of the changes produced by these various treatments, it may be pointed out that they have decreased the toxicity of the two original solutions. The decrease in toxicity is very similar to that observed when extracts of infertile soils are given similar treatment.

The results of adding an organic body.—The beneficial action of certain organic substances has been pointed out in various experiments described in previous bulletins of this Bureau. It was shown, for example, that the addition of 50 parts per million of pyrogallol to an unproductive soil increased the growth of wheat plants 101 per cent. The addition of small amounts (2 to 10 parts per million) of pyrogallol or alpha naphthylamine to the extract of an unproductive soil also had a beneficial effect. Organic substances like the ones mentioned can not be considered as plant nutrients; even if they were, the small amounts added would be insufficient to account for the results produced. Their action may be upon the plant itself, causing it to resist the toxic action of the soil extract, or else these substances, being quite active chemically, act directly upon the toxic substances in the solution.

It became of interest, therefore, to test the action of pyrogallol upon some substance which was known to have a decidedly toxic action upon plants. Cumarin was selected as the substance to be tried, because it had a nearly neutral reaction in aqueous solution. Four series of cultures of wheat plants were set up in solutions containing 75, 50, 25, and 5 parts per million of cumarin, respectively. Half of the cultures received pyrogallol at the rate of 2 parts per million. The other cultures served as controls for comparison. The experiment ran from February 13 to February 23. The following table shows the relative growth of the plants as measured by transpiration during that period:

TABLE III.—*Growth of wheat plants in solutions of cumarin with and without pyrogallol.*

[Growth measured by transpiration and expressed in terms of the growth of controls in distilled water.]

No.	Solutions.	Without pyrogallol.	With pyrogallol.
1	Controls, without cumarin	100	94
2	Cumarin, 75 parts per million.	Dead.	Dead.
3	Same, 50 parts per million	36	82
4	Same, 25 parts per million	82	86
5	Same, 5 parts per million	93	116

These results make it almost certain that pyrogallol had affected the action of the cumarin. The addition of pyrogallol to distilled water was not beneficial to plant growth in this case; in fact, the growth was slightly depressed as the result of its presence. This result speaks against any direct value of the pyrogallol as a nutrient substance. Nevertheless the growth of plants in the cumarin solutions was benefited in each case, and in the solution containing 5 parts per million of cumarin and pyrogallol the growth of plants was distinctly better than in distilled water. In fact, this result would seem to indicate that the pyrogallol had not only been able to overcome the bad effect of the cumarin, but also to convert it into something slightly but distinctly beneficial to growth.

The results of replanting the solutions.—It was shown in a foregoing section that oxidation incident to exposure to air changed tyrosine from a substance having toxic properties to one having beneficial action. From this fact it seemed possible that similar beneficial changes might be wrought in other substances.

The work of Raciborski,[a] has shown that the roots of plants have very definite powers of oxidation, and further work in this laboratory has shown that the roots of wheat plants grown in water culture are capable of quite energetic oxidation. It therefore seemed possible that the solutions in which a crop of wheat seedlings had grown might be less toxic to a second crop because of the oxidation performed by the roots of the first set of plants.

Several solutions were replanted after the first set of plants had been removed. The first crops in the various series were allowed to grow twelve to fourteen days. The growth of the second set showed that in three of the five substances the point at which injury was first noted was lowered, but the concentration necessary to kill the plants had not been altered. The lowest concentrations at which injury was shown in the first and in the second sets of plants were as follows:

TABLE IV.—*Effect of plants in altering the concentrations at which injury was first shown in various toxic solutions.*

[Parts per million.]

No.	Solutions.	Lowest concentrations causing injury.	
		First crop.	Second crop.
1	Arbutin	25	500
2	Cumarin	1	100
3	Cinnamic acid	25	25
4	Sodium cinnamate	100	100
5	Vanillin	50	500

The figures in Table IV show that for certain substances the injurious qualities of the solutions were sensibly altered by the growth of the first set of wheat plants. The arbutin solution, which originally contained 500 parts per million, was so reduced in toxicity by the growth of the first set of plants that it was no more toxic than a fresh solution containing 25 parts per million of arbutin. When cumarin solutions were replanted the solution originally containing 100 parts per million was no more toxic than a freshly prepared solution of 1 part per million. The cinnamic acid solution showed no apparent improvement when used the second time. It was thought that this might have been due to the acid properties of the compound. The experiment was accordingly repeated with sodium cinnamate, which was found by True[a] to be much less toxic to seedlings of *Lupinus albus* than the cinnamic acid. The sodium cinnamate was likewise less toxic to wheat seedlings, but the growth of the first set of wheat plants did not perceptibly alter the point of injury for the second crop. It would seem from this that the activities of the roots were not able to alter sufficiently the properties of cinnamic acid to change its toxicity to seedlings. The question whether the activities of the roots were not modified by the properties of cinnamic acid in such a way that the ameliorating powers were lost seems worthy of more careful studies than we have been able to give it. The toxicity of the vanillin solutions is likewise greatly reduced by the growth of a previous set of plants. A solution which had originally contained 500 parts per million of vanillin was no more toxic to the second set of plants than a freshly prepared solution containing 50 parts per million had been to the first set of plants.

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[a] Bul. Acad. Sci., Cracovie, Math. Naturwiss. Kl., 1905, 338, 668.

The point may be raised, and with some propriety, that the first set of plants absorbed and removed some of the toxic substances from the solutions. While this may be true, it is not likely that the quantities absorbed were sufficient to account for such differences as were noted in the case of arbutin, the concentration of which was so altered that the action of a solution originally containing 500 parts per million was no more injurious than that of a freshly prepared solution containing 25 parts per million. This oxidizing power of roots, described in a previous section, moreover makes it likely that there is an actual chemical change involved as a result of the oxidation.

That the concentration at which injury was manifested was altered, while that at which death occurred was not, is in accord with the assumption upon which the experiment was made. The roots which grew in the stronger solutions were soon seriously injured; hence any power they may have possessed to oxidize or otherwise to ameliorate toxic conditions had a very limited time in which to act.

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[a] Am. Jour. Sci. (4), 9, 183 (1900).

THE EFFECT OF ADDING SUBSTANCES USED AS FERTILIZERS.

In previous publications of the Bureau of Soils it has been pointed out that the beneficial effects of fertilizers are not necessarily due to their content of plant nutrients. The same improvement of growth often results in toxic soil extracts given treatments which do not add any nutrient substances. There is also evidence which indicates that fertilizers may bring about an improvement in conditions by some action upon the substances which previously were detrimental to growth.

To study this matter further, experiments were made in which substances commonly used as fertilizers were added to solutions of toxic substances, which in themselves have a marked toxic action upon wheat, and the effect upon growth noted. Forty plants in four cultures were used for each concentration of the toxic agent employed. The fertilizer salt was added to two of the cultures and comparisons were made with the two which received no fertilizer material. Sodium nitrate and calcium carbonate (lime) were the two substances experimented with. The former is especially efficient in producing improved growth when added to toxic soil extracts. In fact, it produces increased growth in the majority of cases when applied to soils. Calcium carbonate as lime is likewise efficient in improving growth, and is found to be quite generally beneficial when applied with green manures, which are known to contain a variety of organic compounds, some of which have been shown in previous sections of this bulletin to be harmful to plant growth.

Tables V, VI, and VII show the comparative growth of wheat plants in various concentrations of the toxic substances and the effect of the fertilizer salts upon the same. The growth of control plants in pure distilled water is used as the basis for comparison and represented as 100 in each case. Further experiments with cumarin and arbutin were performed, using, however, a smaller range of concentrations, yet the results obtained confirm those in the tables. The cumarin concentrations of 100, 50, and 10 parts per million gave a relative growth respectively of "dead" 47 and 66 without nitrate and "dead" 53 and 105 with 100 parts per million of nitrate added. The arbutin concentrations of 500 and 100 parts per million gave respectively 23 and 41 without nitrates and 27 and 78 with nitrates. It is quite evident from a survey of the results of all these experiments that these fertilizer salts had a beneficial action when added to the toxic solutions, and that the effect was much more marked in the weaker solutions than in the stronger ones. The beneficial effect of calcium carbonate in the cumarin solutions is shown in Plate VI, figure 1. They also indicate that there has been an interaction between the toxic substance and the fertilizer salt added. It may be noted that one of the toxic ubstances (vanillin) produced, in the absence of fertilizer salts, in he lower concentrations what is ordinarily interpreted as stimulaion. The phenomenon of increased growth in the presence of weak oisons is quite general and has been worked out in much detail by Raulin,[a] Richards,[b] Ono,[c] and others.

TABLE V.—*Effect of adding sodium nitrate to toxic solutions of vanillin.*

[Relative growth measured by transpiration.]

o.	Solution.	Without nitrate.	NO_3, 100 parts per million added.
1	Control in distilled water	100	289
2	Vanillin, 500 parts per million	25	34
3	Same, 100 parts per million	53	184
4	Same, 25 parts per million	80	238
5	Same, 10 parts per million	126	246
6	Same, 1 part per million	132	271

TABLE VI.—*Effect of adding calcium carbonate to toxic solutions of cumarin.*

[Relative growth measured by transpiration.]

No.	Solution.	Without carbonate.	Adding $CaCO_3$ 2,000 parts per million.
1	Controls in distilled water	100	153
2	Cumarin, 100 parts per million	Dead.	Dead.
3	Same, 50 parts per million	Dead.	Dead.
4	Same, 25 parts per million	36	58
5	Same, 10 parts per million	74	127
6	Same, 1 part per million	97	166

TABLE VII.—*Effect of adding calcium carbonate to toxic solutions of vanillin.*

[Relative growth measured by transpiration.]

No.	Solution.	Without carbonate.	Adding $CaCO_3$, 2,000 parts per million.
1	Controls in distilled water	100	209
2	Vanillin, 500 parts per million	25	107
3	Same, 100 parts per million	53	127
4	Same, 25 parts per million	80	183
5	Same, 10 parts per million	126	184
6	Same, 1 part per million	132	201

There can be no question that the increased growth in the vanillin cultures of lower concentrations without fertilizers was caused by some stimulating action of the vanillin upon the functions of the plants. Turning now to the columns expressing the effect of the fertilizer salts upon the vanillin, no stimulating effect is noticed. None of the solutions containing vanillin plus a fertilizer salt produced an effect upon growth greater than distilled water containing only the fertilizer salt. In other words, the stimulating effect of the toxic agent totally disappeared. It appears, therefore, that the fertilizer salts had an action upon the toxic organic substances ameliorating the conditions for the growth of plants.

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[a] Ann. Sci. Nat. Bot. (5), **11**, 93 (1869).

[b] Jahrb. wiss. Bot., **30**, 665 (1897); Bul. Torrey Bot. Club, **26**, 463 (1899).

[c] Jour. Coll. Sci. Imp. Univ., Tokyo, **13**, 141 (1900). Hattori, H., ibid., **15**, 371 (1901).

Further evidence on the action of fertilizer salts was gained from the results of replanting the vanillin solutions. The vanillin solutions enumerated in Tables V and VII received a second set of wheat seedlings after the first had been removed. The water lost by transpiration was restored by adding distilled water. The plants were allowed to grow from February 20 to March 1. The behavior of the second set of plants indicates that the conditions for growth were on the whole even better than those existing during the growth of the first set, except in the solution originally containing 500 parts per million vanillin, in which the plants were killed, as in the first planting. The injurious effect of vanillin, as already pointed out, was primarily on the root development of the first crop, and this condition was largely ameliorated by the calcium carbonate and sodium nitrate. In the second crop the root system was, generally speaking, much improved in all three series, including the one without fertilizer salts.

In order to determine whether the growth of the plants was a correct indication of the presence of vanillin the solutions were submitted to a chemical examination.[a] Fairly large quantities of vanillin were shown by this test to be present in the solutions containing no fertilizer salts and originally containing 500 parts per million and 100 parts per million vanillin, while traces only could be found in the solutions originally containing 25 parts per million and 10 parts per million. No vanillin could be demonstrated in any of the solutions in which calcium carbonate or sodium nitrate had been present. That there had been a diminution and even a total disappearance of the toxic substance can not be questioned, because the experiment was repeated several times, always with the same result.

An additional experiment will be described for the purpose of giving a direct comparison between the growth of the first and second set of plants in toxic solutions containing fertilizer salts. Three different solutions were employed in this experiment; the first contained 100 parts per million vanillin, the second 100 vanillin and 100 sodium nitrate, the third 100 vanillin and 2,000 parts per million calcium carbonate. A set of wheat plants was allowed to grow in hese solutions for eight days. The growth of the plants was of the same general character as represented in corresponding treatments n Tables V and VII. After removing the plants from these solutions, the original volumes were restored by the addition of distilled water, to replenish that transpired by the first set of plants, and a second set of seedlings was installed. Nothing was added to the solutions except the distilled water. At the same time a set of plants was installed in a new set of solutions precisely similar in composition to the original set. Accordingly, the plants in the new solutions represented a first crop in toxic solutions containing fertilizers, and the replanted set represented a second crop in the originally similar solutions. The plants in these solutions, together with controls in pure distilled water, were allowed to grow ten days. The relative growth of the plants in the various solutions is given in Table VIII and the plants are represented in Plate VI, figure 2.

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[a] The method used seems to have been first described by Moerk, Am. Jour. Phar. **63**, 572 (1892) and cited in Zeit. anal. Chem., **32**, 242 (1893). It consists in decolorizing the vanillin solution (if necessary) with freshly precipitated lead hydroxide, then adding bromine water drop by drop until a slight excess is present. Ferrous sulphate is finally added until the maximum blue-green color is reached. The test was slightly impaired by the yellow color formed by the reagents in solution to which calcium carbonate had been added, but the presence of sodium nitrate does not interfere with the test. The color was not found to be strictly proportional, although the depth of color produced was approximately indicative of the quantity of vanillin present.

TABLE VIII.—*Relative growth of first and second sets of plants in solutions containing 100 parts per million vanillin, with and without fertilizer substances.*

[The numbers and order of the solutions correspond to those of the plants shown in Plate V, figure 2.]

No.	Solutions.	Relative transpiration.	Relative green weight
1	First crop in vanillin solution	45	100
2	Second crop in vanillin solution	93	103
3	First crop in vanillin solution + $NaNO_3$, 100 parts per million	114	99
4	Second crop in vanillin solution + $NaNO_3$, 100 parts per million	190	135
5	First crop in vanillin solution + $CaCO_3$, 2,000 parts per million	141	111
6	Second crop in vanillin solution + $CaCO_3$, 2,000 parts per million	166	100
7	Controls in pure distilled water	100	100

It will be seen that the results of this experiment confirm those of preceding experiments in showing that toxic properties were ameliorated both by the action of plant roots and by the presence of fertilizer substances. Where the two agencies worked in conjunction, the growth of plants was the best. The second crop naturally showed the better growth in each case owing to the action of the plant roots and fertilizers during the growth of the first crop.

Another experiment upon the action of these fertilizers was performed using arbutin as the toxic substance and growing two sets of plants in the solutions. Arbutin is shown by the figures given in Table I to be decidedly toxic to wheat plants, killing at a concentration of 500 parts per million and injuring at 25 parts per million. As before, sodium nitrate and calcium carbonate were added to the solutions. The set of solutions receiving sodium nitrate was accidentally lost before it was chemically examined for arbutin, and hence does not appear in the records of the second crop. The growth of the plants in this experiment is shown in Table IX, where the figures represent the relative transpiration. The first crop grew eleven days, the second crop ten days.

TABLE IX.—*Relative growth of wheat plants in arbutin solution with and without fertilizer substances.*

No.	Solutions.	Relative transpiration.	
		First crop.	Second crop.
1	Controls in distilled water	100	100
2	Arbutin, 1,000 p. p. m	Dead.	Dead.
3	Same, 500 p. p. m	Dead.	36
4	Same, 200 p. p. m	41	71
5	Same, 100 p. p. m	45	94
6	Same, 50 p. p. m	80	125
7	Same, 1,000 p. p. m. + calcium carbonate 2,000 p. p. m	31	37
8	Same, 500 p. p. m. + calcium carbonate 2,000 p. p. m	51	84
9	Same, 200 p. p. m. + calcium carbonate 2,000 p. p. m	56	74
10	Same, 100 p. p. m. + calcium carbonate 2,000 p. p. m	70	148
11	Same, 50 p. p. m. + calcium carbonate 2,000 p. p. m	92	154
12	Distilled water + calcium carbonate 2,000 p. p. m	109	147
13	Arbutin, 1,000 p. p. m. + sodium nitrate 100 p. p. m	33	....
14	Same, 500 p. p. m. + sodium nitrate 100 p. p. m	53	....
15	Same, 200 p. p. m. + sodium nitrate 100 p. p. m	72	....
16	Same, 100 p. p. m. + sodium nitrate 100 p. p. m	83	....
17	Same, 50 p. p. m. + sodium nitrate 100 p. p. m	91	....
18	Distilled water + sodium nitrate 100 p. p. m	146	....

It will be seen from these figures that the general order of results was the same here as in the preceding experiments where a second set of plants was grown in toxic solutions. The second crop was in all cases better than the first. In making the comparisons it is of course necessary to use the growth in the "replanted" distilled water as the basis of the comparison and not fresh distilled water, since all solutions used for second crops contained the waste products of the first crop. Where the calcium carbonate had been added to the lower concentrations of arbutin, the second crop was remarkably good. These results bear out the results of chemical tests to determine the presence of arbutin.

It was found that diazobenzene-sulphanilic acid reagent[a] could be used as a test for arbutin. While it was only approximately quantitative it gave good indications of the quantities present.

(a) Pauly, Zeit. physiol. Chem., **42**, 508 (1904); **44**, 159 (1905), prepares the diazobenzene-sulphanilic acid in the following way: 2 grams finely pulverized sulphanilic acid are shaken up with 3 cubic centimeters water and 2 cubic centimeters concentrated hydrochloric acid, and this mixture is added in small quantities, within one minute, to a solution of 1 gram of newly prepared potassium nitrite in 1 to 2 cubic centimeters of water; after each addition the mixture is cooled. The sulphanilic acid passes rapidly into solution, and is soon replaced by a dense, white, crystalline deposit of diazobenzene-sulphanilic acid; after a few minutes the fluid part is sucked off and the crystals are then washed with a little water. In testing, sodium carbonate solution is added to the fluid under examination till the reaction is alkaline, and then 3 to 5 cubic centimeters of a freshly prepared solution of a few centigrams of diazo benzene-sulphanilic acid in soda solution.

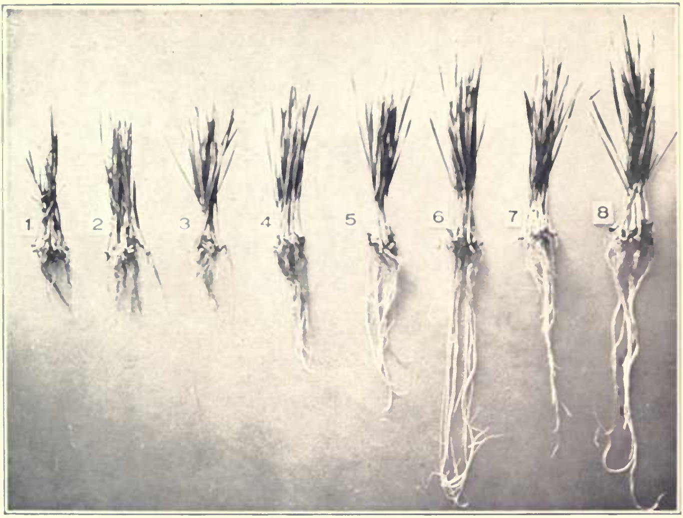

FIG. 1.—EFFECT OF CALCIUM CARBONATE IN OVERCOMING THE TOXIC EFFECT OF CUMARIN.

[Wheat grown in: (1) Solution of cumarin, 25 parts per million; (2) 25 parts + calcium carbonate; (3) 10 parts; (4) 10 parts + calcium carbonate; (5) 1 part; (6) 1 part + calcium carbonate; (7) control in pure distilled water; (8) control in pure distilled water + calcium carbonate.]

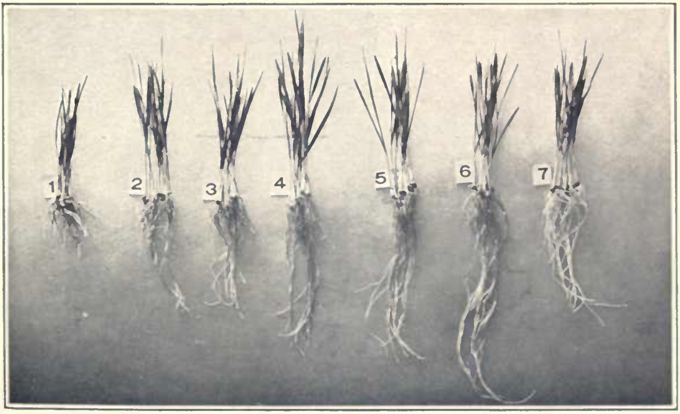

FIG. 2.—EFFECT OF FERTILIZERS IN OVERCOMING THE TOXIC EFFECT OF VANILLIN.

[Wheat grown in: (1) Vanillin solution, first crop; (2) second crop; (3) first crop, vanillin solution + sodium nitrate; (4) second crop, vanillin solution + sodium nitrate; (5) first crop, vanillin solution + calcium carbonate; (6) second crop, vanillin solution + calcium carbonate; (7) control in pure distilled water.]

Pure standard solutions of arbutin are colored bright crimson by he addition of a few drops of diazobenzene-sulphanilic acid reagent. Very weak solutions of arbutin, after the growth of plants, are strongly inged with yellow. The results of the chemical tests made after the growth of the first and second crops are given in Table X.

TABLE X.—*Arbutin remaining in solutions after growth of first and second crops of wheat.*

No.	Solutions.	Results of tests to indicate arbutin	
		After first crop.	After second crop.
1	Originally containing arbutin, 1,000 p. p. m.	Abundant.	Moderate.
2	Originally containing arbutin, 500 p. p. m.	Abundant.	Moderate.
3	Originally containing arbutin, 200 p. p. m.	Moderate.	Weak.
4	Originally containing arbutin, 100 p. p. m.	Weak.	Weak.
5	Originally containing arbutin, 50 p. p. m.	None.	None.
6	Originally containing arbutin, 1,000 p. p. m.+$CaCO_3$ 2,000 p. p. m.	Abundant.	Weak.
7	Originally containing arbutin, 500 p. p. m.+$CaCO_3$ 2,000 p. p. m.	Moderate.	Weak.
8	Originally containing arbutin, 200 p. p. m.+$CaCO_3$ 2,000 p. p. m.	Weak.	Trace.
9	Originally containing arbutin, 100 p. p. m.+$CaCO_3$ 2,000 p. p. m.	Trace.	None.
10	Originally containing arbutin, 50 p. p. m.+$CaCO_3$ 2,000 p. p. m.	None.	None.

An inspection of these results shows that the calcium carbonate has had the same action upon arbutin as the fertilizer salts used in the previous experiments had upon vanillin. There had been a disappearance of arbutin from the solutions in which plants grew, but much more had disappeared from solutions containing the fertilizer salt.

The question next arises as to how these toxic substances were caused to disappear. Three possibilities seem to present themselves: (1) The plants themselves absorbed part of the toxic substance and oxidized some of it; (2) the fertilizer ingredients had a chemical action upon the toxic substance; (3) both plants and fertilizer salts acted together, either directly or indirectly, upon the toxic substance.

The first possibility was tested by the experiments in which a second set of plants was grown in the toxic solutions. It was there shown that the plants did have an ameliorating action, although they were only able to remove entirely the toxic substances in the lowest concentrations.

The second possibility, viz, that the fertilizer substances had a direct action upon the toxic substance, was tested by the following experiment: A solution containing 100 parts per million of vanillin was prepared; a portion of it received sodium nitrate equivalent to 100 parts per million of NO_3, and another portion received calcium carbonate at the rate of 2,000 parts per million. These solutions were then allowed to stand eight days. At the end of that time another set of solutions, exactly similar to the first, was prepared.

They were therefore compared by cultivating plants in them and using the growth of the plant as an indicator of the amount of toxic substance present in each solution. It was thought that any action the fertilizers might have had would be shown by the growth of the plants in these solutions. The results of the experiment are presented in tabular form in Table XI.

TABLE XI.—*Relative growth, measured by green weight, of wheat plants in solutions of vanillin treated with fertilizer salts at different times.*

No.	Solution.	Solutions prepared at time of planting.	Solutions prepared eight days before planting.
1	Controls in distilled water	100	100
2	Vanillin, 100 parts per million	85	70
3	Same, + $NaNO_3$, 100 parts per million	99	92
4	Same, + $CaCO_3$, 2,000 parts per million	111	170

It will be seen from these figures that the 8-day action of the salts on the solution is somewhat contradictory. The solutions to which nitrate had been added was certainly not improved by standing this length of time. Those to which calcium carbonate had been added were, on the other hand, quite appreciably improved by standing, thus suggesting that this substance aids independently in overcoming the toxic properties of the vanillin.

In regard to the third possibility it might be pointed out that the experimental data thus far presented go to show that plants themselves can by their growth ameliorate the toxic conditions slightly, also that certain fertilizer treatments may bring about some improvement due probably to direct action on the substance, but far greater beneficial effects are produced by the combined action of plant and fertilizer salt. In other words, the plant and the fertilizer ingredients working together are able to accomplish more in the way of destroying toxic substance than either can do working alone. That such a substance as vanillin is destroyed does not admit of doubt if any conclusion is to be drawn from the experiments previously recorded. Whether the destruction of vanillin as such took place in the solution or within the cells of the wheat plants was not ascertained, but it probably takes place in the solution. This may be safely inferred from the behavior of the plants. Vanillin itself has a very inhibitive action upon the growth of the roots of wheat seedlings in water culture (Plate III, fig. 1). All plants grown in vanillin solutions showed more harmful effects in the growth of roots than in the growth of tops. When, however, the fertilizer salts were added in sufficient amount to ameliorate distinctly the conditions or growth, the improvement in root development was relatively as great or even greater than in that of the tops.

A large number of experiments showing the benefits derived from he action of fertilizers on soils have been presented in Bulletin 40 of this Bureau and will not be presented in detail here. The results of the experiments here mentioned indicate that the small yields of unproductive soils can be greatly improved by treatments which remove or destroy toxic substances in those soils. In the experiments in which succeeding crops were grown in the same soil it was shown that certain fertilizers may act very beneficially upon soils containing toxic materials excreted from the plant roots.

It has been pointed out that methods of cultivation which promote the aeration of the soil and the growth of micro-organisms, may aid in destroying deleterious organic substances. The undue accumulation of such substances can also be prevented by proper and systematic crop rotation. In all these practices it is known that the addition of suitable fertilizers plays an important part in bringing about the destruction of harmful organic substances and consequent improvement of soil conditions. In other words, the experiments which showed that unproductiveness arises from the presence in soils of the waste products of plants have been supplemented by other experiments showing that fertilizer salts can actually bring about or aid in the destruction of toxic organic substances. It seems reasonable, therefore, to conclude that the benefits derived from fertilizers may, at least in part, be due to their direct or indirect action upon toxic organic substances in soils.

Attention may be again called to the fact that pot experiments in which fertilizers were employed to overcome the effects of replanting similarly show that certain fertilizers are able to destroy the toxic waste products of plant growth and to improve soil conditions. It was shown in the experiments mentioned that the ameliorating power does not necessarily depend upon the amount of plant nutrients which a fertilizer contains.

Summing up the results of experiments upon the amelioration of toxic conditions it appears that there are numerous ways in which such unfavorable conditions may be overcome. The toxic solutions were markedly improved by treatments similar to those which benefit the extracts of unproductive soils. Treatment with absorbing agents or brief boiling was beneficial. The toxic solutions were greatly improved after one set of wheat plants had been grown in them. Undoubtedly there was some toxic material directly absorbed by the first set of plants, but the amount was entirely too small to account for the diminished toxicity of the solutions when the second set of plants was grown. The vanillin solution, for example, was so reduced in toxicity that a solution originally containing 500 parts per million was no more toxic to the second set of plants than a solution of 50 parts per million was to the first. It has been found that an equal number of wheat plants can remove in a similar length of time not more than 30 to 50 parts per million of nitrates from solution and there is no reason to believe that toxic substances should be removed at a much more rapid rate. The oxidizing powers of the roots therefore appear to be able to act upon the toxic organic materials in such a way that their toxic properties are lost. The large amount of root surface which most plants possess makes this oxidizing power an important one in relation to soil conditions and especially in relation to the destruction of toxic conditions through crop rotation.

In the experiments described it was shown that while the plants alone and fertilizer substances alone were able to accomplish a partial destruction of the toxic substances the combined action of plants and substances ordinarily employed as fertilizers caused a much greater destruction of toxic material and consequent improvement in growth.

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U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF SOILS—BULLETIN No. 48.

MILTON WHITNEY, Chief.

FERTILITY OF SOILS AS AFFECTED BY MANURES.

BY

FRANK D. GARDNER.

WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1908.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., June 24, 1907.

Sir: I have the honor to transmit a manuscript entitled Fertility of Soils as Affected by Manures, by Frank D. Gardner, in charge of Soil Management. It embodies the results of a uniform scheme of manurial treatments, as measured by the resulting increase in plant growth on soils collected from 220 fields in 23 States, located in the eastern half of the United States.

The increasing use of manures, and especially of commercial fertilizers, by the farmers of the United States is sufficient justification for careful investigations as to the relative efficiency of various forms of manures on different soils. You will find here a vast amount of data, treated in a manner commensurate with the importance of the subject. It should be of great value to all who are interested in the use of manures.

The manuscript has been gone over carefully with Assistant Secretary Hays, who concurs in my recommendation for its publication as Bulletin No. 48 of the Bureau of Soils.

Respectfully,

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

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FERTILITY OF SOILS AS AFFECTED BY MANURES.[a]

INTRODUCTION.

The use of manures as a means of increasing the growth of crops dates back to ancient times. At the time of the discovery of America, the North American Indians used dead fish as a manure for corn. The Peruvians have used guano since the beginning of their recorded history, and the Chinese have long recognized the value of all kinds of excrements as fertilizers. In the early part of the last century De Saussure established the existence of the mineral constituents of the soil in plants, and while he believed that they were essential to the life of plants, his contemporaries regarded them as nonessential, or at the best useful only as a kind of stimulant.

Justus Von Liebig, as a result of his investigations, published in 1843 a new edition of his notable work, "Chemistry in its Application to Agriculture and Physiology," in which it may be said he laid the foundation of the celebrated "mineral theory" of agriculture.

Prior to the time of Liebig the use of manures and fertilizers was purely an art, the beneficial results of which had not been satisfactorily explained. Liebig's mineral plant food theory, apparently so ample, and in time widely accepted, attributed the beneficial effect of fertilizers solely to the plant food constituents which were supplied to the growing plants, and thereby laid the foundation for the compounding of fertilizers to meet the needs of soils and crops. There soon sprang into existence a soil chemistry which had for its object an investigation of the stores of plant food in soils with a view to ascertaining the agricultural value of lands, as well as the character and amount of fertilizer, if any, that would give the largest net crop income per acre. It was soon learned that the soil constituents existed in various forms or compounds not all of which were available as plant food, and this led to a study of inexpensive methods of determining the available constituents, a study which has formed no small part of soil chemistry even down to the present time, with little indication that a method will ever be devised that will prove universally satisfactory for all soils and crops.

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[a] A comparative study of the fertility of the soils of the central and eastern United States, as influenced by manures and fertilizers and measured by the paraffin-pot method.

So far as can be gleaned from the writings of soil investigators, only within recent years have any considerable number of them come to realize that there is no definite relation between the available plant food constituents of soils, as determined by mineral analysis, and their crop-yielding capacities. Neither had they arrived at that further realization that the crop-yielding capacity of a soil is dependent upon a complexity of factors, any one of which may be dominant, but all of which are concerned in large or small degree.

Arable soils contain the organic remains of previous crops together with excretions produced during their growth and are also filled with living forms. Their bacterial flora is diversified and the activities and processes which take place within the soil, physical, chemical, and biological, are exceedingly complex, and at present but imperfectly understood. It is the sum total of these activities and their products that determines largely the fitness of a soil for plants, rather than the variation in the character and composition of its mineral matter. While manure and fertilizers may often increase crop yields as a result of a direct supply of plant food or as a stimulant to the plants, there is now abundant evidence that their effect is rather the result of a direct action upon the soil, thereby changing its relation to plants. Complex and imperfectly understood as is this action, it is a more satisfactory explanation of the benefits derived from fertilizers than the idea that the inconsequential amounts of nitrogen, potash, and phosphorus applied, as compared with the larger stores of those elements already in the soil, should be directly responsible for such marked increase in growth as frequently follows the application of fertilizers.

The prime object of manuring the soil, whether with stable manure, green manure, or commercial fertilizers, is to increase its crop-yielding capacity, and in order to justify the practice the resulting increase in product must be more than enough to offset the cost of the fertilizers applied. That is to say, the beneficial effect on the present and succeeding crops must be sufficient to compensate for the cost of the fertilizers and give a profit on the capital so invested.

The first noteworthy use of commercial fertilizers in the United States was in 1848, during which year there was imported 1,000 tons of guano. This was followed the succeeding year by twenty times that quantity, after which date the importation steadily increased until 1880, when it reached its maximum and began to fall off because of a failing supply. Other materials, notably sodium nitrate from Chile and the potash salts from Germany, have taken the place of the failing supply of guano, and these, together with the development of our phosphate mines, the use of cotton-seed meal, and the utilization of slaughterhouse by-products, have met the continually increasing demand for commercial fertilizers by our farmers. According to our census reports, the expenditure for fertilizers in the United States in 1880 was $28,500,000. Ten years later it was $38,500,000, and in 1900 it reached the significant sum of $54,750,000. There seems little doubt that this rate of increase in the use of fertilizers will continue for some time to come, and the subject is one of sufficient national importance to justify careful investigations.

OBJECT OF THE INVESTIGATION.

The object of this investigation is not for the purpose of explaining how fertilizers act nor of studying the relation of the composition of the soil to the beneficial effect of the fertilizer when applied to it, but rather to compare the effects of several high-grade standard fertilizer ingredients, lime, stable manure, and cowpea vines when applied under like conditions to a large number of soils, collected from widely separated areas and representing a wide range in soil texture, type, origin, and crop adaptation. By making a comparative test of a large number of soils it was thought that there might be established a relation between the manurial requirements and the origin, formation, type, or crop adaptation of the soil.

While there has been recorded in agricultural literature, in the aggregate, a large number of field tests of fertilizers on a great variety of soils, representing nearly every State in the eastern half of the United States, it is impossible to make a satisfactory comparison of the results obtained, because of the innumerable details in which the conditions of the tests do not agree. The variation in the amount, class, kind, and composition of the fertilizer used, the time and manner of its application, the test crop used, and the weather conditions which prevailed form such a wide range of possible combinations that it is rare to find two tests that are strictly comparable.

In the present investigation the same variety of wheat was used throughout as the test crop, and all of the conditions for growth, excepting the manurial treatments to be tested, were maintained as nearly uniform as possible. With the same fertilizer ingredients, in like form and used in the same combinations, for a crop common to all, the results obtained from this large number of soils are strictly comparable, and far exceed in number any similar tests that can be brought together on such a basis.

Mention should also be made of the fact that all tests reported in the following tables under areal surveys—and they constitute fully four-fifths of them—were made for the further purpose of gaining practical knowledge concerning the manurial requirements of the principal soil types as established by the soil survey parties and with the ultimate object of determining what manures or fertilizers would give best results on the soils. The results of all such tests are reported in general terms in the soil survey reports for the respective areas in which they occur.

THE SOILS.

The soils tested in this investigation, 220 in number, represent 90 types, half that number of soil series, and many geological formations. The samples were taken from twenty-three States, extending from the Mississippi River to the Atlantic seaboard and from Rhode Island to Texas. With the exception of a limited number of miscellaneous samples, the greater number were collected from areas that were in process of being surveyed by the Bureau of Soils during the summer of 1905, and the following winter, and are representative of the soils of those areas rather than the vast expanse of country included in the twenty-three States above mentioned. Each sample, being a composite, made up of fifteen or twenty small samples, taken from different parts of the same field, is representative of the field from which it is taken as well as the type which it represents. The samples were placed in strong grain bags and shipped to the Bureau's headquarters, where they were at once transferred to covered galvanized iron cans for storage. In this way the original condition and original moisture content were, as far as practicable, maintained until they could be tested. This is important in relation to the test, for it has been found by experience that as a result of long storage and resulting air-dry condition soils become more productive and are usually less responsive to fertilizers than when such a change is prevented.

THE METHOD.

The paraffin-pot method, described in Circular No. 18 of this Bureau and in the appendix to Farmers' Bulletin No. 257 of the United States Department of Agriculture, was employed in these tests, and while it is not designed to supersede field tests, results obtained with it, when compared with results obtained on the same soils at the agricultural experiment stations in Rhode Island,[a] New York, Ohio,[b] Iowa, Missouri, and North Carolina, show that it will indicate the manurial requirements of soils for general farm crops with a fair degree of accuracy. It is also admirably adapted to an investigation of the character described in the following pages.

The soil to be tested is thoroughly pulverized by crushing all lumps, and if containing stone or gravel this is removed by sifting. The sample is then thoroughly mixed and equal amounts weighed into granite-ware pans, where they receive their respective applications of manure or fertilizers and are made up to their optimum water content with distilled water. After remaining in the pans for about a week, being occasionally wet with distilled water, and frequently stirred in order to secure a thorough incorporation of the fertilizer and a good soil condition, it is ready to pot and plant. Five small wire-gauze pots are used for each treatment. About 350 grams of soil is then placed in each pot, uniformly packed, and planted with six selected germinated kernels of wheat, after which the pots are dipped in melted paraffin, which not only forms an intimate contact with the soil but makes the pot water tight. The soil is then covered with a thin layer of washed quartz sand and the pot and contents weighed and weight recorded. The pots are next placed in trays and given a favorable exposure in the greenhouse for three or four days or until the plants attain a height of about 1½ inches, at which time the pots are sealed. The sealing consists of covering the tops with paraffined paper disks in which are slits through which the plants grow. The disks are sealed to the sides of the pots by means of melted paraffin. The loss of water by direct evaporation from the soil is in this way reduced to a negligible quantity.

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[a] See Bul. 109 of the Rhode Island Expt. Sta.

[b] See Buls. Nos. 167 and 168 of the Ohio Agricultural Expt. Sta.

During the growing of the plants, which usually continues from eighteen to twenty-one days from the date of sealing, the pots are weighed at intervals of two or three days and watered with distilled water in order to retain a favorable moisture content for plant growth. By this method the loss of water or the amount transpired by the plants may be ascertained periodically, and at the end of the experiment the total amount of water given off through the plants of each pot obtained for comparison with the growth and green weight of the plants, which is ascertained by cutting and weighing the plants at the time the experiment is concluded. All conditions of the experiment are so carefully controlled that the average result of five pots rarely differs more than 5 per cent from the average result of any other five pots that have been treated throughout in precisely the same manner (see Table I). Differences which occur beyond this amount may therefore safely be attributed to the different manurial treatments which have been given. This method has several advantages over the growing of plants in open and porous pots. The method of coating the soil with paraffin prevents any accumulation of roots between the soil and the receptacle, a trouble which is common in pot experiments. The complete sealing up of the soil also enables the experimenter to determine the amount of water which the plant has actually used and transpired in its process of growth, and this, together with the small size of the pots, enables the moisture content and its fluctuations to be carefully controlled.

On good soils, or as a result of favorable treatment, plants are produced in the little pots in twenty-five days or less time, the green weight of which sometimes equals or exceeds 1 per cent of the weight of the soil in which they grew. Such plants are approximately 85 per cent water; they have transpired about 100 units of water for each unit of green matter produced, and their dry matter is relatively richer in mineral constituents and nitrogen than that of mature plants. On this basis, an acre foot of soil, weighing 3,500,000 pounds, would produce 35,000 pounds of green matter, requiring for its production the equivalent of 17½ inches of rainfall. This green matter would be equivalent to 5,900 pounds of air-dry material, or about 50 bushels of wheat and 1½ tons of straw to an acre. While the removal of green matter equal to 1 per cent of the soil in the little pots is somewhat above the average, it serves as an illustration of the heavy draft made upon the soil in a very short time, a draft, as regards moisture and mineral constituents, although part of the latter comes from the seed, greater than that which takes place under field conditions by the removal of a large mature crop, assuming that the removal takes place to a depth not greater than 1 foot, which for wheat and similar crops would be approximately correct, and providing also the movement of plant food by capillarity from below 1 foot be ignored.

TABLE I.—*Actual transpiration in grams for each of twenty pots, on three soils, under uniform treatment, and the percentage variation from the average for each pot, also average percentage variation of each group of five pots.*

Leonardtown loam. Corn.			Cecil clay—poor.			Leonardtown loam.		
Transpiration.	Variation.		Transpiration.	Variation.		Transpiration.	Variation.	
For each pot.	For each pot.	For 5 pots.	For each pot.	For each pot.	For 5 pots.	For each pot.	For each pot.	For 5 pots.
Grams.	*Per cent.*	*Per cent.*	*Grams.*	*Per cent.*	*Per cent.*	*Grams.*	*Per cent.*	*Per cent.*
69.9	− 5.5	−0.9	39.3	+10.1	−2.8	87.5	+ 0.4	+3.3
77.6	+ 4.9		25.7	−28.0		90.5	+ 3.9	
58.7	−20.1		37.7	+ 5.6		89.1	+ 2.2	
83.5	+12.8		34.8	− 2.5		98.4	+12.9	
76.5	+ 3.3		35.9	+ 0.6		84.8	− 2.6	
59.1	−20.2	−3.0	35.8	+ 0.3	+4.1	89.9	+ 3.2	+1.6
72.1	− 2.6		37.3	+ 4.4		99.2	+13.9	
79.2	+ 7.0		38.6	+ 8.1		87.7	+ 0.7	
73.9	− 0.2		35.4	− 0.8		80.5	− 7.6	
74.1	+ 0.8		38.9	+ 8.9		85.2	− 2.2	
82.3	+11.1	+2.2	38.8	+ 8.6	+0.8	79.8	− 8.4	−2.7
66.8	− 9.8		33.6	− 5.9		79.5	− 8.7	
70.6	− 4.6		37.8	+ 5.9		86.1	− 1.1	
68.9	− 6.9		38.1	+ 6.7		88.8	+ 1.9	
89.9	+21.4		31.7	−11.2		89.5	+ 2.7	
84.3	+13.8	+2.0	34.7	− 2.8	−2.5	82.4	− 5.4	−2.1
79.0	+ 6.7		32.3	− 9.5		83.0	− 4.7	
76.4	+ 3.2		39.8	+11.2		94.3	+ 8.2	
68.3	− 7.7		36.9	+ 3.4		87.4	+ 0.3	
69.7	− 5.8		31.2	−12.6		79.3	− 8.9	

FERTILIZERS USED.

In this investigation the tests were confined to the use of high-grade, standard fertilizing materials, consisting of nitrate of soda, sulphate of potash, and acid phosphate, together with air-slaked lime, well-decomposed stable manure, and green cowpea vines. These ingredients were applied to the soil separately and in various combinations as follows:

Treatment and rate per acre.

1. Untreated.
2. Manure, 10 tons.
3. Lime, 1 ton.
4. Nitrate of soda, 200 pounds.
5. Sulphate of potash, 200 pounds.
6. Acid phosphate, 200 pounds.
7. Nitrate of soda and sulphate of potash, 200 pounds each.
8. Nitrate of soda and acid phosphate, 200 pounds each.
9. Sulphate of potash and acid phosphate, 200 pounds each.
10. Nitrate of soda, sulphate of potash, and acid phosphate, 200 pounds each.
11. Same, plus lime, 2,000 pounds.
12. Cowpea vines 5 tons, lime 2,000 pounds.

The rate of application is based on the weight of an acre of soil to the depth of 7 inches, which is approximately 2,000,000 pounds. The fertilizers were applied in solution, and the lime, manure, and cowpea vines in bulk, each being finely ground.

CALCULATION OF RESULTS.

While this report combines the results of more than 13,000 pots, individual record of which has been made, the results were reported on forms, of which the following is a sample:

[Can 101.]

Actual transpiration and green weight and relative transpiration and green weight of 30 wheat plants on the basis of 100 for the untreated soil.

Soil: Norfolk Sandy Loam. Locality: Waycross, Ga.
Planted: April 5. Sealed April 10. Disctd.: April 28. Basket Nos.: 2006–2125.

Number.	Treatment and parts per million.[a]	Transpiration, 18 days.	Green weight.	Relative variation by—	
				Transpiration.	Green weight.
1	Untreated	757.6	7.0	100	100
2	Manure 10,000	1295.2	14.2	171	203
12	Cowpeas 5,000, lime 1,000	1135.7	13.6	150	194
10	Nitrate of soda, potassium sulphate, and acid phosphate 100 each	1160.3	11.5	153	164
11	Same + lime 1,000	1090.1	11.0	144	157
7	Nitrate of soda and potassium sulphate 100 each	1047.2	10.8	139	154
8	Nitrate of soda and acid phosphate 100 each	997.6	9.6	132	137
4	Nitrate of soda 100	1053.0	9.5	139	136
5	Potassium sulphate 100	925.9	8.0	122	114
9	Potassium sulphate and acid phosphate 100 each	833.6	8.0	110	114
3	Lime 1,000	803.0	7.0	106	100
6	Acid phosphate 100	651.9	6.5	86	93

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[a] Parts per million multiplied by 2 equals the pound rate per acre on the basis of 2,000,000 pounds as the weight of an acre of soil 7 inches deep.

On this form are given the total transpiration and total weight of green plants for each treatment, consisting of five pots. The transpiration and the green weight of plants for each treatment are entered in the third and fourth columns, respectively, while the relative transpiration and weight, based on 100 for the untreated soil, are given in the fifth and sixth columns and are merely computed from the actual transpiration and weight in order to convert the comparison to a percentage basis and make it more simple.

The variation by transpiration, while a good indication of the relative growth and effect of the treatments, frequently gives a range of lesser magnitude than the actual growth of plants. Plants that have made a marked increase in growth as a result of soil treatment usually contain a higher percentage of water than untreated ones and therefore show a slightly lesser variation by dry, or water-free, weight than by green weight. See Table II, which follows. The increase in growth is also accompanied by an improvement in condition which can only be measured by appearance, but which will usually prove an advantage to the better plants if grown to maturity. The results given in this bulletin are all based on the actual green weight of plants, the weighings being made immediately upon cutting the plants and under uniform conditions.

TABLE II.—*Percentage gain or loss attributable to various fertilizer treatments on four soils.*

[P=acid phosphate. K=sulphate of potash. N=nitrate of soda. L=lime. M=stable manure.]

A.—BASED ON GREEN WEIGHT OF PLANTS GROWN ON UNTREATED SOILS.

Soil.	Green weight of plants grown on untreated soils.	Percentage gain or loss attributable to—									
		P.	K.	N.	PK.	PN.	KN.	PKN.	L.	PKNL.	M.
	Grams.										
Cecil clay, good	8.8	0	− 2	− 4	......	9	14	− 4	5	....	9
Cecil clay, poor	8.8	− 1	1	0	......	− 6	7	5	6	....	−14
Leonardtown loam, good	8.3	16	7	47	......	41	47	46	10	....	17
Leonardtown loam, poor	6.5	− 7	15	8	......	0	12	22	1	....	24
Average	7.6	2	5	13	......	11	20	17	5	....	9

B.—BASED ON DRY WEIGHT OF PLANTS GROWN ON UNTREATED SOILS.

Soil.	Dry weight of plants grown on untreated soils.	Percentage gain or loss attributable to—									
		P.	K.	N.	PK.	PN.	KN.	PKN.	L.	PKNL.	M.
	Grams.										
Cecil clay, good	1.60	− 1	−11	− 9	......	− 1	3	13	−5	....	−11
Cecil clay, poor	1.55	− 3	− 4	0	......	− 8	8	5	−1	....	−17
Leonardtown loam, good	1.20	13	4	37	......	25	47	36	8	....	18
Leonardtown loam, poor	1.22	2	18	5	......	0	9	24	6	....	9
Average	1.39	3	2	8	......	4	17	19	2	....	0

ARRANGEMENT AND TABULATION OF RESULTS.

Table III, which follows, gives the actual green weight of plants grown on the untreated soils and the percentage increase or decrease in growth, the latter indicated by the minus (–) sign, resulting from the various fertilizer ingredients and combinations. The data are arranged by States, areas, and types and averages are given for areas and for types within areas. The symbols at the head of the columns are used for the sake of brevity. **P** stands for acid phosphate; **K** for sulphate of potash; **N** for nitrate of soda; **L** for air-slaked lime; **M** for well-rotted stable manure, and **Cv** for green cowpea vines. The ingredients and rate of application are given in the preceding form. All data resulting from the tests are embodied in Table III. Marked variations from the general trend are exceptional and most frequently occur with manure or cowpea vines. These substances have occasionally given negative results apparently as a result of decomposition products from which the soil did not have sufficient time to recover prior to the planting of the seed. The blanks in the table indicate no tests for the ingredients or combinations heading the columns in which they occur. Practically all such omissions occurred in miscellaneous samples which were tested by the Bureau parties at several of the State experiment stations. Table III gives the results for 220 soils and from these results many tabulations were made, parts of which are given on subsequent pages. The arrangement and segregation of data in subsequent tables are for the purpose of a further comparative study of the facts as well as to enable the reader to verify statements that may follow in the text, although a number of facts are given from tabulations other than those which follow.

TABLE III.—*Percentage increase in growth attributable to the various fertilizer applications.*

Soil type and locality.	Weight of plants grown on untreated soil.	Gain or loss attributable to—										
		P.	K.	N.	PK.	PN.	KN.	PKN.	L.	PKNL.	M.	CvL.
WISCONSIN.												
Portage County:	*Grams.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Miami stony sand.....	9.9	6	13	11	– 3	11	21	22	– 3	19	47	8
Miami sand...........	6.0	7	15	33	5	24	29	39	7	43	80	– 4
Miami sandy loam.....	9.0	4	8	2	– 1	10	14	3	4	21	29	12
Marshall gravelly loam	11.0	– 1	– 2	14	2	3	16	4	2	3	36	14
Marshall sand.........	8.4	7	9	31	13	23	32	35	11	8	34	3
Portage silt loam......	10.0	–11	– 9	– 6	– 1	–10	– 3	3	5	10	21	10
Portage silt loam......	8.7	2	–16	– 2	5	– 9	10	1	9	–14	42	–14
Average for area....	9.0	2	3	12	3	7	17	15	5	13	41	4
MISSOURI.												
Crawford County:												
Clarksville silt loam...	6.6	26	15	17	27	25	15	7	14	1	43	32
Wabash silt loam......	7.6	–11	1	– 3	– 2	3	– 5	– 1	0	2	23	24
Clarksville stony loam.	14.6	4	3	– 2	– 9	2	11	3	– 3	– 2	–10	13
Average for area....	9.6	6	6	4	5	10	7	3	4	0	19	23

TABLE III.—*Percentage increase in growth attributable to the various fertilizer applications*—Continued.

Soil type and locality.	Weight of plants grown on untreated soil.	Gain or loss attributable to—										
		P.	K.	N.	PK.	PN.	KN.	PKN.	L.	PKNL.	M.	CvL.
MISSOURI—continued.												
Scotland County:	*Grams.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Shelby silt loam	9.6	7	24	14	22	17	32	28	11	28	69	30
Miscellaneous:												
Loess, McBain County	7.8	8	22	28	26	26	47	50	19	....	23	35
Clay loam, Salem	7.0	.....	.....	.....	25	50	60	68	25	50	57	35
Silt loam, Columbia	5.9	.....	.....	.....	29	54	44	61	7	66	34	50
INDIANA.												
Newton County:												
Marshall fine sandy loam	6.3	5	12	9	0	5	12	−4	−12	−1	60	−2
Marshall loam	7.6	17	22	17	20	14	21	16	22	21	77	34
Clyde fine sand	12.6	−21	−2	−14	−8	−23	13	−17	−12	−7	32	−4
Average for area	8.8	0	11	4	4	−1	15	−2	−1	4	56	9
Tippecanoe County:												
Marshall silt loam	7.2	4	1	6	10	.....	3	12	−7	6	−2	4
Marshall loam	7.5	−3	2	7	−6	4	18	6	−3	7	42	−2
Miami silt loam	5.6	30	21	28	26	58	46	58	17	35	71	30
Average for area	6.8	10	8	14	10	31	22	25	2	16	37	11
OHIO.												
Westerville area:												
Miami black clay loam	8.3	−11	6	−2	9	13	7	8	1	11	22	5
Miami clay loam	6.1	11	5	15	3	27	11	13	7	11	15	45
Miami loam	8.6	−8	3	−2	−3	1	8	−5	2	2	48	15
Average for area	7.8	−3	5	4	3	14	9	5	3	8	28	22
Miscellaneous:												
Volusia silt loam, Wooster	5.8	0	.....	.....	14	47	46	62	21	76	52	.....
Miami clay loam, Germantown	7.1	4	.....	.....	6	24	30	27	9	47	10	22
Miami clay loam, Strongsville	....	−4	−5	12	−9	−6	−6	−6	30	....	9	.....
NEW YORK.												
Tompkins County:												
Dunkirk clay loam	9.0	0	9	13	−1	6	23	11	−14	12	68	−5
Dunkirk clay loam	4.5	−18	4	55	−5	27	47	42	29	....	33	54
Average for type	6.8	−9	7	34	−3	17	35	27	8	....	51	25
Dunkirk loam	8.4	−4	2	15	−1	16	20	12	−7	11	46	0
Miami stony loam	9.6	4	1	1	−4	−8	6	11	0	7	36	26
Average for area	7.9	−5	4	21	−3	10	24	19	2	10	46	19
Binghamton area:												
Dunkirk gravelly sandy loam	6.6	4	1	11	4	20	16	1	26	27	29	69
Dunkirk gravelly loam	10.6	9	9	1	−8	0	9	7	−3	−11	20	−9
Wabash loam	10.6	−1	11	5	16	12	22	26	10	15	31	10
Average for area	9.3	4	7	6	4	11	16	11	11	10	27	23
Other localities in State:												
Volusia silt loam	5.4	2	15	13	11	8	38	20	9	32	51	29
Volusia silt loam	4.8	−2	15	34	15	21	53	35	15	62	81	.....
Volusia silt loam	6.6	4	22	10	11	4	19	23	8	15	77	13
Dunkirk clay loam	8.9	16	29	20	31	10	21	28	19	22	17	28
Dunkirk clay loam	10.2	11	11	18	−5	−6	6	5	8	0	17	21

TABLE III.—*Percentage increase in growth attributable to the various fertilizer applications*—Continued.

Soil type and locality.	Weight of plants grown on untreated soil.	Gain or loss attributable to—										
		P.	K.	N.	PK.	PN.	KN.	PKN.	L.	PKNL.	M.	CvL.
PENNSYLVANIA.												
Montgomery County:	*Grams.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Hagerstown loam.....	10.3	13	− 2	1	11	13	6	9	6	23	20	29
Penn silt loam.........	12.3	8	12	8	11	11	24	13	− 8	4	24	36
Lansdale silt loam....	9.9	0	23	1	27	− 7	31	7	19	17	9	30
Chester loam.........	7.8	0	9	4	21	18	15	27	4	33	13	8
Average for area....	10.1	5	10	4	18	9	19	14	5	19	17	24
RHODE ISLAND.												
The State:												
Miami silt loam, Kingston..........	3.6	− 8	−19	−14	28	22	22	31	133	111	39	......
Miami stony loam, Middleton..........	7.8	......	......	......	......	......	......	18	9	41	......	......
Miami stony loam, Jamestown..........	5.8	......	......	......	......	......	......	24	60	94	......	......
Miami stony loam, Curtis Corners..........	6.7	......	......	......	......	......	......	7	5	45	......	......
Miami stony loam, Woonsocket..........	9.1	......	......	......	......	......	......	10	10	17	......	......
Miami stony loam, Little Compton.....	15.4	......	......	......	......	......	......	5	0	8	......	......
Miami stony loam, Ashaway..........	5.6	......	......	......	......	......	......	4	21	35	......	......
Average for type....	8.4	......	......	......	......	......	......	11	18	40	......	......
Gloucester stony loam, East Greenwich.....	8.7	......	......	......	......	......	......	15	2	37	......	......
Gloucester stony loam, Chepachet..........	8.5	......	......	......	......	......	......	4	9	21	......	......
Gloucester stony loam, Tarkiln..........	11.4	......	......	......	......	......	......	3	0	0	......	......
Gloucester stony loam, Foster..........	8.5	......	......	......	......	......	......	2	25	14	......	......
Gloucester stony loam, Greene..........	7.2	......	......	......	......	......	......	−22	8	30	......	......
Average for type..	8.9	......	......	......	......	......	......	0	9	20	......	......
Alton stony loam, Hope Valley..........	5.5	......	......	......	......	......	......	34	38	54	......	......
Alton stony loam, Wickford..........	4.7	......	......	......	......	......	......	51	− 2	51	......	......
Average for type..	5.1	......	......	......	......	......	......	43	18	53	......	......
Warwick sandy loam, Alton..........	7.1	......	......	......	......	......	......	41	− 8	42	......	......
Warwick sandy loam, Barrington..........	7.2	......	......	......	......	......	......	23	28	42	......	......
Average for type..	7.2	......	......	......	......	......	......	32	10	42	......	......
Average for area..	7.9	......	......	......	......	......	......	15	14	35	......	......
VIRGINIA.												
Louisa County:												
Cecil sandy loam......	7.2	24	5	13	31	13	27	30	5	39	25	57
Cecil loam............	4.6	36	47	75	26	75	100	102	71	153	63	158
Average for area....	5.9	30	26	44	28	44	64	66	38	96	44	108
Hanover County:												
Wickham sandy loam.	7.5	− 3	5	11	−1	10	16	36	9	35	31	−12
Norfolk sandy loam...	7.5	3	11	20	16	17	35	30	− 1	47	44	− 8
Average for area....	7.5	0	8	16	8	14	26	33	4	41	38	10

TABLE III.—*Percentage increase in growth attributable to the various fertilizer applications*—Continued.

Soil type and locality.	Weight of plants grown on untreated soil.	Gain or loss attributable to—										
		P.	K.	N.	PK.	PN.	KN.	PKN.	L.	PKNL.	M.	CvL.
VIRGINIA—continued.												
Appomattox County:	*Grams.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Cecil clay	12.9	.....	.....	6	−13	4	12	2	− 1	2	− 3	24
Cecil clay, Pocahontas field	11.7	− 3	4	− 3	− 2	.....	.....	9	− 6	7	− 2	7
Cecil clay, Mitchell field	13.2	− 7	.....	4	3	.....	.....	6	5	− 4	2	6
NORTH CAROLINA.												
New Hanover County:												
Norfolk sand	4.1	37	41	122	61	124	131	151	66	154	241	144
Norfolk fine sand	6.4	3	9	37	20	45	51	63	16	70	94	37
Norfolk fine sandy loam	7.3	3	3	22	3	20	33	29	8	31	57	34
Portsmouth fine sand	3.0	13	30	77	40	87	117	110	70	173	130	230
Average for area	5.2	14	21	65	31	69	83	88	40	107	131	111
Miscellaneous:												
Cecil clay (good), Statesville	8.8	0	− 2	− 4	.....	9	14	− 4	5	.....	9	.....
Cecil clay (poor), Statesville	8.8	− 1	1	0	.....	− 6	7	5	6	.....	−14	3
Cecil clay, Iredell test farm	4.5	86	34	42	99	97	35	105	45	105	90	.....
Cecil sandy loam, Raleigh	4.1	20	31	30	29	23	39	49	52	103	53	54
Iredell clay loam, Statesville	5.2	7	21	16	19	9	28	34	− 1	28	33	.....
Norfolk fine sandy loam, Edgecombe	4.8	44	42	63	33	52	71	56	25	77	66	.....
Norfolk fine sandy loam Tarboro	3.0	25	22	42	29	51	59	63	1	70	38	78
Porters clay, Asheville	5.8	− 6	− 2	29	−14	24	40	19	10	53	8	15
Porters clay, Biltmore	12.4	11	15	18	16	26	11	25	31	26	61	24
Porters sandy loam, Blantyre	4.5	4	44	20	31	20	51	24	43	22	61	31
Portsmouth sand, Pinehurst	4.8	42	26	42	35	43	38	56	26	46	41	45
Portsmouth silt loam, Chowan County	4.5	2	19	14	16	23	62	62	19	57	46	74
Silt loam, Union County	4.6	− 4	0	32	19	19	21	42	4	51	28	.....
Tobacco soil, Wake County	4.7	9	11	28	20	17	22	30	11	16	.....	.....
SOUTH CAROLINA.												
York County:												
Cecil sand	3.9	−15	− 8	26	28	8	20	54	8	71	90	60
Cecil sandy loam	7.0	40	3	28	− 9	0	40	34	33	41	76	58
Iredell clay loam	7.7	0	6	19	1	6	16	18	3	17	51	19
Average for area	6.2	8	0	24	7	5	25	35	15	43	72	46
Cherokee County:												
Cecil clay	7.4	− 4	− 6	36	− 2	26	39	35	4	44	42	12
Cecil silt loam	6.6	2	1	52	9	47	52	48	39	56	81	74
Cecil fine sandy loam	5.9	− 3	7	46	− 1	46	46	52	29	68	88	123
Cecil sandy loam	6.9	−12	28	35	9	33	60	58	4	65	71	5
Iredell clay loam	9.1	− 3	7	32	1	27	46	27	14	42	36	7
Average for area	7.2	− 4	7	40	3	36	49	44	18	55	64	44
Lancaster County:												
Cecil silt loam	7.3	.....	.....	75	15	63	61	67	8	73	10	111
Miscellaneous:												
Orangeburg sandy loam, St. Matthews	11.8	0	− 2	15	5	16	14	26	19	28	25	17
Portsmouth sandy loam, Darlington	5.3	.....	.....	13	9	35	26	30	40	105	44	138

TABLE III.—*Percentage increase in growth attributable to the various fertilizer applications*—Continued.

Soil type and locality.	Weight of plants grown on untreated soil.	Gain or loss attributable to—										
		P.	K.	N.	PK.	PN.	KN.	PKN.	L.	PKNL.	M.	CvL.
TENNESSEE.												
Henderson County:	*Grams.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Lexington silt loam....	7.5	1	1	36	5	16	44	36	5	57	72	17
KENTUCKY.												
McCracken County:												
Memphis silt loam....	5.0	− 3	3	39	8	25	42	42	18	48	70	− 2
GEORGIA.												
Waycross area:												
Norfolk sand, 12 miles west Waycross......	5.5	− 9	24	45	27	49	65	72	64	109	124	118
Norfolk sand, 4½ miles SE. Waycross.......	5.6	− 4	30	61	18	45	50	57	20	121	114	132
Norfolk sand, 3½ miles NW. Waltertown ...	6.1	− 2	− 5	36	5	22	41	24	34	55	77	65
Average for type....	5.7	− 5	16	47	17	39	52	51	39	95	105	105
Norfolk fine sand, 3 miles W. Waycross..	6.1	7	15	55	23	49	69	74	34	84	102	107
Norfolk fine sand, 8 miles SE. Waycross.	6.0	5	8	53	− 2	18	38	50	27	32	113	107
Norfolk fine sand, 2 miles W. Waycross..	7.4	− 9	− 8	− 3	− 6	−12	0	14	6	25	28	36
Average for type ..	6.5	1	5	35	5	18	36	46	22	47	81	83
Norfolk Sandy loam, 2½ miles N. Waycross..............	7.0	− 7	14	36	14	37	54	64	0	57	103	94
Norfolk sandy loam, 3 miles NW. Waycross..............	6.5	11	15	54	15	77	102	85	35	100	109	109
Norfolk sandy loam, 2½ miles SW. Elsie....	5.0	0	16	20	3	15	42	25	− 9	43	54	42
Average for type..	6.2	1	15	37	11	43	66	58	9	67	89	82
Norfolk fine sandy loam, 5¼ miles W. Waycross...........	7.5	17	28	60	23	63	83	73	40	89	113	113
Norfolk fine sandy loam, 3 miles E. Waycross...........	7.9	1	5	29	6	21	38	24	22	35	96	67
Norfolk fine sandy loam, 4 miles N. Manor..............	3.9	11	29	74	35	51	79	86	64	105	150	176
Average for type..	6.4	10	21	54	21	45	67	61	42	76	120	119
Portsmouth fine sand, 5¼ miles SE. Waycross..............	5.2	6	21	73	31	92	104	77	29	117	150	148
Portsmouth fine sand, 1 mile S. Needham....	5.2	1	15	50	26	75	80	90	92	153	219	175
Portsmouth fine sand, 1 mile S. Glenmore...	5.5	2	18	33	24	33	29	71	20	75	64	109
Average for type..	5.3	3	18	52	27	67	71	79	47	115	144	144
Average for area...	6.0	2	15	45	16	42	59	59	32	80	108	107
FLORIDA.												
Escambia County:												
Portsmouth sand......	8.3	2	5	12	5	18	11	11	48	48	47	35
Norfolk sand..........	5.4	16	18	13	11	11	13	11	46	74	83	107
Norfolk sand..........	5.9	5	32	45	15	20	84	46	24	55	94	97
Norfolk sand..........	7.2	4	19	33	9	16	41	22	29	23	66	65
Average for type...	6.2	8	23	30	12	16	46	26	33	51	81	90

TABLE III.—*Percentage increase in growth attributable to the various fertilizer applications*—Continued.

Soil type and locality.	Weight of plants grown on untreated soil.	Gain or loss attributable to—										
		P.	K.	N.	PK.	PN.	KN.	PKN.	L.	PKNL.	M.	CvL.
FLORIDA—continued.												
Escambia County—Cont'd.	*Grams.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Norfolk fine sandy loam	8.4	−7	14	15	8	−12	−4	11	35	14	32	51
Norfolk fine sandy loam	5.5	10	12	−5	32	39	30	32	45	82	32	85
Norfolk fine sandy loam	3.3	24	36	27	33	48	12	48	136	130	90	136
Average for type	5.7	9	21	12	24	25	13	30	72	75	51	91
Average for area	6.3	8	19	20	16	20	27	26	52	61	63	82
ALABAMA.												
Lee County:												
Cecil sandy loam	8.6	1	9	14	−2	8	31	15	10	28	.....	58
Cecil sandy loam	5.6	−11	−7	29	−11	13	11	43	13	52	43	.....
Average for type	7.1	−5	1	21	−7	10	21	29	12	40	.....	.....
Norfolk sand	6.8	9	10	40	3	63	77	62	57	103	107	160
Norfolk sand	4.7	−1	−1	30	−3	21	40	35	50	135	108	143
Average for type	5.8	4	4	35	0	42	58	48	53	119	108	151
Norfolk sandy loam	6.1	−14	4	42	15	37	43	46	11	64	42	104
Norfolk sandy loam	7.7	12	19	55	20	50	53	63	19	87	61	164
Average for type	6.9	−1	12	48	18	43	48	54	15	75	52	134
Norfolk coarse sand	5.3	−7	15	48	8	34	49	50	5	70	59	101
Norfolk coarse sand	6.4	−12	0	20	−2	3	13	25	22	23	33	41
Average for type	5.8	−9	7	34	3	18	31	37	13	46	46	71
Average for area	6.4	−3	6	35	3	28	40	42	23	70	65	110
Miscellaneous:												
Clarksville clay loam, Florence	11.5	.....	.....	6	−4	−4	3	19	−1	10	−15	−13
Clarksville silt loam, Florence	9.5	.....	.....	25	17	13	17	20	4	15	−3	30
Orangeburg clay, Kings farm	10.3	3	6	17	6	40	19	19	16	35	32	26
Orangeburg clay, Ford's farm	9.1	22	24	42	37	45	34	67	20	55	49	35
Orangeburg sandy loam, Rawl's farm	8.1	6	−5	4	5	9	2	12	21	17	17	20
Orangeburg sandy loam, Marion	4.8	14	7	25	19	59	28	69	12	69	37	60
MISSISSIPPI.												
Pontotoc County:												
Lufkin clay	6.4	8	8	28	6	22	14	28	6	31	9	48
Lufkin silt loam	5.4	41	44	52	32	39	44	50	63	56	37	78
Orangeburg clay	6.6	−9	3	18	0	14	27	45	−3	47	18	32
Orangeburg sandy loam	7.6	17	−2	28	2	10	21	26	6	39	25	24
Monroe silt loam	8.0	−4	−6	13	6	23	25	14	9	18	29	39
Average for area	6.8	10	9	28	9	22	26	32	16	38	24	44
Montgomery County:												
Orangeburg fine sandy loam	7.5	24	20	43	13	53	53	48	24	64	60	60
Lintonia loam	8.5	7	17	29	27	17	26	22	24	16	30	48

TABLE III.—*Percentage increase in growth attributable to the various fertilizer applications*—Continued.

Soil type and locality.	Weight of plants grown on untreated soil.	Gain or loss attributable to—										
		P.	K.	N.	PK.	PN.	KN.	PKN.	L.	PKNL.	M.	CvL.
MISSISSIPPI—continued.												
Montgomery Co.—Cont'd.	*Grams.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Memphis silt loam.....	10.6	−13	− 3	− 2	−16	0	7	1	−1	16	−4	6
Memphis silt loam.....	9.5	−16	− 9	0	− 8	− 7	8	− 5	−5	3	−5	11
Memphis silt loam.....	8.6	−13	6	12	3	10	14	13	6	9	6	34
Memphis silt loam.....	10.2	− 3	− 2	−15	− 6	5	9	12	1	20	18	28
Memphis silt loam.....	11.2	−10	− 7	−11	−10	−13	5	8	0	−3	5	9
Memphis silt loam.....	7.0	7	9	14	4	14	12	14	13	17	36	40
Average for type....	9.5	− 7	− 2	− 2	− 6	0	11	7	3	11	9	21
Average for area...	9.3	− 1	3	8	0	9	18	14	8	18	18	30
LOUISIANA.												
Caddo Parish:												
Caddo fine sandy loam.	4.4	18	18	86	25	16	84	36	18	52	20	186
Caddo fine sandy loam.	5.0	−10	4	33	− 4	2	62	4	8	72	44	148
Caddo fine sandy loam.	8.8	− 7	5	7	− 8	15	2	9	8	14	6	41
Caddo fine sandy loam.	6.0	6	17	26	− 4	20	12	8	19	16	79	23
Average for type...	6.0	2	11	38	2	13	40	14	13	39	37	100
Miller fine sand.......	5.8	12	12	38	3	24	21	19	22	34	81	48
Miller fine sand.......	7.3	21	26	10	21	38	17	1	14	16	43	36
Average for type....	6.6	17	19	24	12	31	19	10	18	25	62	42
Norfolk fine sand......	3.7	− 3	51	62	65	54	65	51	41	113	146	195
Norfolk fine sand......	5.4	21	19	41	5	61	62	56	39	80	92	98
Norfolk fine sand......	5.3	15	21	32	36	32	61	59	9	74	28	80
Average for type...	4.8	11	30	45	35	49	63	55	30	89	89	124
Norfolk fine sandy loam................	8.7	4	9	7	9	17	21	9	0	30	9	25
Norfolk fine sandy loam................	9.6	− 8	9	13	−19	8	13	− 1	6	19	22	1
Norfolk fine sandy loam................	5.6	− 3	20	35	19	76	44	33	28	54	54	52
Norfolk fine sandy loam................	7.9	1	− 5	−10	3	16	44	35	2	56	18	47
Average for type....	8.0	− 1	8	11	3	29	31	19	9	40	26	31
Orangeburg fine sand..	7.4	8	10	21	8	15	28	21	20	28	15	28
Orangeburg fine sand.	5.0	−22	−10	−10	−10	20	14	28	12	50	114	124
Average for type....	6.2	− 7	0	6	− 1	18	21	25	16	39	115	76
Orangeburg fine sandy loam................	6.5	3	3	0	0	10	7	15	7	15	20	26
Orangeburg fine sandy loam................	5.0	0	6	10	22	20	30	32	0	44	34	96
Average for type....	5.7	2	5	5	11	15	19	24	4	30	27	61
Average for area....	6.3	3	13	24	10	26	35	24	15	45	54	74
ARKANSAS.												
Prairie County:												
Calhoun clay..........	8.3	12	12	14	12	16	16	26	18	27	4	13
Crowley silt loam......	7.1	− 8	0	9	9	0	−2	7	36	60	19	38
Crowley silt loam......	10.1	− 1	3	0	− 6	− 5	−2	3	2	5	7	9
Crowley silt loam......	7.0	0	10	43	− 6	22	26	27	43	71	64	80
Crowley silt loam......	8.1	9	14	2	− 3	7	13	0	46	33	18	42
Average for type....	8.1	0	7	14	− 1	6	9	9	32	42	27	42

TABLE III.—*Percentage increase in growth attributable in the various fertilizer applications*—Continued.

Soil type and locality.	Weight of plants grown on untreated soil.	Gain or loss attributable to—										
		P.	K.	N.	PK.	PN.	KN.	PKN.	L.	PKNL.	M.	CvL.
ARKANSAS—continued.												
Prairie County—Cont'd.	*Grams.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Morse clay	8.8	− 9	8	1	2	11	6	0	6	− 7	6	22
Morse clay	10.8	4	− 3	2	− 7	2	6	− 3	2	4	4	9
Morse clay	11.1	5	13	− 3	4	3	9	−11	− 7	− 1	5	4
Average for type	10.2	0	6	0	0	5	7	− 5	0	− 1	5	12
Acadia silt loam	11.2	0	4	29	11	25	24	27	12	33	46	27
Acadia silt loam	7.3	1	7	10	12	1	10	15	14	37	7	16
Acadia silt loam	7.4	22	20	29	31	18	22	41	23	48	31	38
Acadia silt loam	9.0	0	11	6	11	31	26	18	−11	41	32	21
Average for type	8.7	6	11	19	16	19	21	25	10	40	29	26
Waverly silt loam	6.5	15	20	27	27	15	31	38	61	55	38	54
Waverly silt loam	7.8	− 7	9	− 7	− 3	− 4	4	− 3	37	40	18	41
Waverly silt loam	5.0	28	20	18	23	22	29	28	104	150	10	132
Average for type	6.4	12	16	13	16	11	21	21	67	82	22	76
Average for area	8.3	5	10	12	8	11	15	14	26	40	21	36
TEXAS.												
San Marcos area:												
Blanco loam	8.7	17	21	19	21	23	10	33	20	21	28	37
Crawford silt clay	9.2	20	21	31	20	40	29	22	20	42	40	52
Crawford silt clay	9.2	− 7	2	19	− 1	8	19	23	4	31	14	34
Crawford silt clay	8.8	13	25	30	18	29	30	42	24	46	56	11
Average for type	9.1	9	16	27	12	26	26	29	16	40	37	32
Houston black clay	7.9	8	8	21	8	23	9	30	15	21	30	42
Houston black clay	8.9	0	4	15	17	4	9	17	5	23	8	23
Houston black clay	7.0	20	21	31	25	33	35	35	17	42	10	38
Houston black clay	8.1	− 4	− 5	21	5	12	21	19	6	26	25	32
Average for type	8.0	6	7	22	14	18	19	25	11	28	18	34
Average for area	8.5	8	12	23	14	22	20	28	14	32	26	34
Rusk County:												
Caddo fine sandy loam	8.2	6	2	53	5	51	53	47	7	47	61	57
Caddo fine sandy loam	8.1	12	11	40	15	43	35	34	17	36	62	40
Average for type	8.2	9	7	47	10	47	44	40	12	42	62	49
Norfolk fine sand	8.5	14	16	41	16	29	54	49	21	55	86	48
Norfolk fine sand	7.8	− 4	8	21	6	17	28	28	3	60	103	69
Norfolk fine sand	8.6	5	6	19	− 3	21	36	36	10	26	61	37
Average for type	8.3	5	10	27	6	22	39	38	11	47	83	51
Norfolk fine sandy loam	7.5	20	28	38	41	42	62	65	21	64	105	62
Norfolk fine sandy loam	6.1	31	31	48	48	52	56	48	40	41	48	80
Average for type	6.8	26	30	43	45	47	59	57	31	53	76	71
Orangeburg fine sandy loam	9.2	−12	− 6	14	− 9	− 6	14	36	13	39	68	53
Orangeburg fine sandy loam	9.2	0	2	34	− 1	26	26	26	12	37	37	66
Orangeburg fine sand	7.5	− 7	20	31	24	27	39	40	8	60	80	68
Susquehanna fine sandy loam	7.0	− 3	0	9	− 3	3	3	9	−11	26	29	36
Average for area	8.0	6	11	32	13	28	37	38	13	45	67	54

TABLE III.—*Percentage increase in growth attributable to the various fertilizer applications*—Continued.

Soil type and locality.	Weight of plants grown on untreated soil.	Gain or loss attributable to—										
		P.	K.	N.	PK.	PN.	KN.	PKN.	L.	PKNL.	M.	Cv.
TEXAS—continued.												
Miscellaneous:												
	Grams.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Galveston clay, Galveston	11.2	−14	−12	3	−23	− 9	4	−20	− 2	− 8	4	31
Houston black clay loam, San Antonio	5.8	8	1	− 5	14	12	35	10	11	19	19	− 7
Orangeburg clay, Maroney's farm	8.6	− 3	1	17	− 3	12	7	14	4	5	29	5
Orangeburg fine sandy loam, Crockett	8.3	......	......	67	17	60	67	92	24	93	19	58
Orangeburg fine sandy loam, Palestine	9.8	......	......	30	− 7	37	31	21	7	32	−14	40
Orangeburg fine sandy loam, Nagadoches	8.8	1	6	31	10	31	43	24	16	24	56	15
Orangeburg fine sandy loam, Palestine	11.4	− 7	− 4	11	− 8	10	14	14	−15	9	37	43
IOWA.												
Miscellaneous:												
Wisconsin drift (good)	9.6	−10	15	30	−13	34	42	52	− 5	....	47	......
Wisconsin drift (poor)	7.7	19	34	53	30	49	79	82	17	....	86	......
Iowan drift	9.0	16	25	28	25	47	27	57	36	....	69	......
Missouri loess	11.6	0	2	15	......	......	......	......	......	....	5	......
South Iowan loess	5.4	......	......	......	35	32	39	41	17	....	−17	47
Kansan till	5.9	7	15	48	12	57	83	73	6	42	24	......
ILLINOIS.												
Marion silt loam	7.7	−13	− 8	− 3	−11	− 4	9	− 8	−13	− 4	48	−12
Red silt loam	7.0	3	8	19	8	17	24	22	16	38	26	45
NEW JERSEY.												
Miscellaneous:												
Norfolk sandy loam, Woodbine	6.0	12	5	20	− 2	16	34	20	2	17	25	14
Norfolk fine sandy loam, Woodbine	6.5	1	1	9	9	22	35	32	7	31	28	42
CONNECTICUT.												
Connecticut Valley area:												
Hartford sandy loam	8.2	......	......	18	3	− 6	18	3	10	29	14	58
MARYLAND.												
Miscellaneous:												
Leonardtown loam (good)	8.3	16	7	47	......	41	47	46	10	....	17	......
Leonardtown loam (poor)	6.5	− 7	15	8	......	0	12	22	1	....	24	89
Muck, peat, and swamp soils:												
Illinois	9.4	16	49	4	39	14	40	25	7	33	45	51
Iowa	15.0	24	26	21	11	− 4	15	20	−14	....	64	......
Wisconsin, Portage County	7.2	42	25	21	51	20	39	47	23	41	51	16
Indiana, Newton County	4.4	−25	61	14	66	− 7	41	100	14	70	40	18
Virginia, Portsmouth	3.2	53	112	69	65	84	75	69	75	97	47	72
Average for type	7.8	22	55	26	47	25	42	52	21	60	49	39

COMPARATIVE EFFICIENCY OF SALTS USED SEPARATELY AND IN COMBINATION.

Table IV, which follows, is primarily for the purpose of showing the wide variation in the aggregate effect of the three fertilizer ingredients when used separately as compared with their efficiency when used together. This table gives the percentage increase or decrease in growth (the latter indicated by the minus sign) produced by acid phosphate, sulphate of potash, and nitrate of soda used separately; the aggregate increase attributable to these three ingredients; the increase when the three ingredients were combined and the difference between the aggregate and that observed when the same ingredients were used in combination. All soils having complete data for these observations are included, the total number being 190, and the data are arranged in a descending series, beginning with the greatest difference in favor of the sum of the ingredients, until the difference becomes zero, after which the series is ascending and the differences are in favor of the combination. A wide variation is shown in the last column, the difference ranging from a maximum of 165 per cent in favor of the sum of the ingredients to zero and then increasing to a maximum of 72 per cent at the other extreme in favor of the combination.

Of the total number of comparisons (190) there are 71 soils in which the efficiency of the combination exceeded the aggregate of the separate ingredients, 117 soils in which the aggregate of the individual effects exceeds that of the combination, and 2 soils in which the aggregate effect of the single ingredients exactly equals the increase in growth when those ingredients were used in combination. The number of soils that show very wide differences in respect to the aggregate efficiency of the ingredients as compared with the effect when the same ingredients are combined is small, the number increasing greatly as the lesser differences are approached. For example, 60 soils show differences of 9 per cent or less, while for 115 soils the difference is within the limit of 19 per cent. Within this limit of 19 per cent there are 51 soils in which the difference is in favor of the combination and 62 in which it is in favor of the aggregate increase for the same ingredients used separately. (See Table V following.) As a result of averages within these limits, acid phosphate gives an increase of 0.64 per cent, sulphate of potash 6.68 per cent, and nitrate of soda 19 per cent, or a total of 26.32 per cent, as compared with 24.5 per cent as a mean effect of the same ingredients used in combination on the same soils. Within these limits, which includes 60 per cent of the soils, the average efficiency of the ingredients as measured by the growth of the plants is nearly the same whether used separately or in combination. It therefore appears that each ingredient has performed special functions which differ from and are independent of those performed by the others, whether the ingredients are applied separately or in combination.

Of the soils in which the effect of the ingredients in combination differs from the aggregate effect of the same ingredients used separately by 20 per cent or more, 55 are in favor of the ingredients used separately and 20 in favor of their combination. Within the former group of soils there are 15 instances in which the aggregate increase of the ingredients when used separately is more than three times as great as when the same ingredients were used in combination, and 12 instances where the aggregate is less than three times but more than two times as great as when used in combination. Within this group, therefore, the function of the several ingredients is to a considerable degree identical, at least so far as they effect an increase in the growth of plants, and one may be substituted for another to a considerable extent.

Of the soils in which the efficiency of the combination exceeds that of the same ingredients used separately by 20 per cent or more there are only 20. In this group the function of each ingredient is not only different from that of the others, but each is dependent upon the presence of others in order that it may have the greatest effect.

There is no apparent relation either by soil type or locality with this grouping of the soils; neither do the soils of one group appear to be particularly more responsive to the complete fertilizer than those of another. Of 190 observations on each, the individual ingredients give negative results as follows: Acid prosphate 66 times, sulphate of potash 31 times, and nitrate of soda 22 times. The combination of all three ingredients gives a negative result only 9 times, while the aggregate effect of the individual ingredients becomes negative 21 times.

Table V shows the average increase produced by each ingredient, the aggregate increase, and the actual increase when the ingredients were combined for soils in which the aggregate increase from individual ingredients differs within certain limits from that obtained when the same ingredients were combined.

There are ten soils in which each of the three ingredients when used separately gave a greater increase in growth than when all were combined and ten others in which two of the three each equaled or exceeded the gain produced by the three combined. (See Tables VI and VII.) These soils are not confined to particular localities or types, neither are they associated with high or low degree of natural fertility, as may be seen by the wide range in weight of plants on the untreated soils.

TABLE IV.—*Percentage increase in growth attributable to P, K, and N, and the sum of the same, as compared with the observed increase when a mixture of the three fertilizers was applied.*

[Results arranged in descending series, beginning with the greatest actual difference in favor of the sum of the ingredients.]

State.	Locality.	Soil.	Weight of plants on untreated soil.	Increase attributable to—			Sum of P, K, and N.	Increase attributable to PKN.	Difference.
				P.	K.	N.			
			Grams.	*P.ct.*	*P.ct.*	*P.ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Virginia	Portsmouth	Peat	3.2	53	112	69	234	69	165
North Carolina.	Edgecombe	Norfolk fine sandy loam.	4.8	44	42	63	149	56	93
Mississippi	Pontotoc County.	Lufkin silt loam	5.4	41	44	52	137	50	87
Louisiana	Caddo Parish	Caddo fine sandy loam.	4.4	18	18	86	122	36	86
Texas	Rusk County	Norfolk fine sandy loam.	6.1	31	31	48	110	48	62
Louisiana	Caddo Parish	Norfolk fine sand	3.7	−3	51	62	110	51	59
North Carolina.	Iredell test farm.	Cecil clay	4.5	86	34	42	162	105	57
Virginia	Louisa County	Cecil loam	4.6	36	47	75	158	102	56
Louisiana	Caddo Parish	Miller fine sand	7.3	21	26	10	57	1	56
North Carolina.	Pinehurst	Portsmouth sand	4.8	42	26	42	110	56	54
Missouri	Crawford County.	Clarksville silt loam.	6.6	26	15	17	58	7	51
Iowa	Ames	Peat	15.0	24	26	21	71	20	51
Texas	San Marcos	Crawford silt clay	9.2	20	21	31	72	22	50
North Carolina.	New Hanover County.	Norfolk sand	4.1	37	41	122	200	151	49
North Carolina.	Blantyre	Porter's sandy loam.	4.5	4	44	20	68	24	44
Illinois	Manito	Muck	9.4	16	49	4	69	25	44
Louisiana	Caddo Parish	Miller fine sand	5.8	12	12	38	62	19	43
Louisiana	Caddo Parish	Caddo fine sandy loam.	6.0	6	17	26	49	8	41
Wisconsin		Muck	7.2	42	25	21	88	47	41
Indiana	Newton County	Marshall loam	7.6	17	22	17	56	16	40
Mississippi	Montgomery County.	Orangeburg fine sandy loam.	7.5	24	20	43	87	48	39
Florida	Escambia County.	Norfolk fine sandy loam.	3.3	24	36	27	87	48	39
Arkansas	Prairie County	Waverly silt loam.	5.0	28	20	18	66	28	38
Texas	San Marcos area	Houston black clay.	7.0	20	21	31	72	35	37
South Carolina.	York County	Cecil sandy loam	7.0	40	3	28	71	34	37
New York	Geneseo	Dunkirk clay loam.	8.9	16	29	20	65	28	37
Florida	Escambia County.	Norfolk sand	5.9	5	32	45	82	46	36
Florida	Escambia County.	Norfolk sand	5.4	16	18	13	47	11	36
New York	Genesee County	Dunkirk clay loam.	10.2	11	11	18	40	5	35
Florida	Escambia County.	Norfolk sand	7.2	4	19	33	56	22	34
Georgia	Waycross area	Norfolk fine sandy loam.	7.5	17	28	60	105	73	32
North Carolina.	Raleigh	Cecil sandy loam	4.1	20	31	30	81	49	32
Mississippi	Montgomery County.	Lintonia loam	8.5	7	17	29	53	22	31
Arkansas	Prairie County	Acadia silt loam	7.4	22	20	29	71	41	30
Indiana	Newton County	Marshall fine sandy loam.	6.3	5	12	9	26	−4	30
Georgia	Waycross area	Norfolk sand	5.6	−4	30	61	87	57	30
Texas	Rusk County	Caddo fine sandy loam.	8.1	12	11	40	63	34	29
Georgia	Waycross area	Norfolk fine sandy loam.	3.9	11	29	74	114	86	28
North Carolina.	Tarboro	Norfolk fine sandy loam.	5.3	25	22	42	89	63	26
Texas	San Marcos area	Crawford silt clay	8.8	13	25	30	68	42	26
Arkansas	Prairie County	Crowley silt loam	7.0	0	10	43	53	27	26
Arkansas	Prairie County	Morse clay	11.1	5	13	−3	15	−11	26
Louisiana	Caddo Parish	Norfolk fine sand	5.4	21	19	41	81	56	25
Arkansas	Prairie County	Crowley silt loam	8.1	9	14	2	25	0	25
Iowa	Ames	Wisconsin drift (poor).	7.7	19	34	53	106	82	24
Arkansas	Prairie County	Waverly silt loam.	6.5	15	20	27	62	38	24
Texas	San Marcos	Blanco loam	8.7	17	21	19	57	33	24
Maryland	Leonardtown	Leonardtown loam (good).	8.3	16	7	47	70	46	24
Georgia	Waycross area	Portsmouth fine sand.	5.2	6	21	73	100	77	23
Alabama	Lee County	Norfolk sandy loam.	7.7	12	19	55	86	63	23
Louisiana	Caddo Parish	Caddo fine sandy loam.	5.0	−10	4	33	27	4	23

TABLE IV.—*Percentage increase in growth attributable to P, K, and N, and the sum of the same, etc.*—Continued.

State.	Locality.	Soil.	Weight of plants on untreated soil.	Increase attributable to— P.	Increase attributable to— K.	Increase attributable to— N.	Sum of P, K, and N.	Increase attributable to PKN.	Difference.
			Grams.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Texas	Rusk County	Norfolk fine sand	8.5	14	16	41	71	49	22
Alabama	Ford's farm	Orangeburg clay	9.1	22	24	42	88	67	21
Texas	Rusk County	Norfolk fine sandy loam.	7.5	20	28	38	86	65	21
Indiana	Tippecanoe County.	Miami silt loam	5.6	30	21	28	79	58	21
Louisiana	Caddo Parish	Norfolk fine sandy loam.	5.6	−3	20	35	52	33	19
North Carolina	Biltmore farm	Porters clay	12.4	11	15	18	44	25	19
North Carolina	Wake County	Tobacco soil	4.7	9	11	28	48	30	18
Louisiana	Caddo Parish	Orangeburg fine sand.	7.4	8	10	21	39	21	18
Ohio	Westerville area	Miami clay loam	6.1	11	5	15	31	13	18
Mississippi	Pontotoc County	Orangeburg sandy loam.	7.6	17	−2	28	43	26	17
New Jersey	Woodbine	Norfolk sandy loam.	6.0	12	5	20	37	20	17
Missouri	Scotland County	Shelby silt loam	9.6	7	24	14	45	28	17
Pennsylvania	Montgomery County.	Lansdale silt loam	9.9	0	23	1	24	7	17
Georgia	Waycross	Norfolk fine sand	6.0	5	8	53	66	50	16
Wisconsin	Portage County	Miami sand	6.0	7	15	33	55	39	16
Mississippi	Pontotoc County	Lufkin clay	6.4	8	8	28	44	28	16
Mississippi	Montgomery County.	Memphis silt loam	7.0	7	9	14	30	14	16
Pennsylvania	Montgomery County.	Penn silt loam	12.3	8	12	8	28	13	15
New York	Binghamton area.	Dunkirk gravelly sandy loam.	6.6	4	1	11	16	1	15
Louisiana	Caddo Parish	Norfolk fine sandy loam.	9.6	−8	9	13	14	−1	15
Texas	Rusk County	Caddo fine sandy loam.	8.2	6	2	53	61	47	14
Texas	Nagadoches	Orangeburg fine sandy loam.	8.8	1	6	31	38	24	14
New York	....	Volusia silt loam	6.6	4	22	10	36	23	13
Iowa	....	Iowan drift	9.0	16	25	28	69	57	12
New York	....	Volusia silt loam	4.8	−2	15	34	47	35	12
Wisconsin	Portage County	Marshall sand	8.4	7	9	31	47	35	12
Virginia	Louisa County	Cecil sandy loam	7.2	24	5	13	42	30	12
Arkansas	Prairie County	Calhoun clay	8.3	12	12	14	38	26	12
New York	Binghamton area	Dunkirk gravelly loam.	10.6	9	9	1	19	7	12
Georgia	Waycross area	Norfolk fine sandy loam.	7.9	1	5	29	35	24	11
Florida	Escambia County	Norfolk fine sandy loam.	8.4	−7	14	15	22	11	11
New York	Tompkins County	Dunkirk clay loam	9.0	0	9	13	22	11	11
Louisiana	Caddo Parish	Norfolk fine sandy loam.	8.7	4	9	7	20	9	11
Wisconsin	Portage County	Miami sandy loam	9.0	4	8	2	14	3	11
Georgia	Waycross area	Norfolk sandy loam.	5.0	0	16	20	36	25	11
North Carolina	New Hanover County.	Portsmouth fine sand.	3.0	13	30	77	120	110	10
North Carolina	Statesville	Iredell clay loam	5.2	7	21	16	44	34	10
Texas	Rusk County	Orangeburg fine sandy loam.	9.2	0	2	34	36	26	10
New York	....	Volusia silt loam	5.4	2	15	13	30	20	10
Louisiana	Caddo Parish	Norfolk fine sand	5.3	15	21	32	68	59	9
South Carolina	Cherokee County	Iredell clay loam	9.1	−3	7	32	36	27	9
Alabama	Lee County	Cecil sandy loam	8.6	1	9	14	24	15	9
Ohio	Strongsville	Miami clay loam	....	−4	−5	12	3	−6	9
Illinois	Pulaski	Red silt loam	7.0	3	8	19	30	22	8
Wisconsin	Portage County	Miami stony sand	9.9	6	13	11	30	22	8
Florida	Escambia County	Portsmouth sand	8.3	2	5	12	19	11	8
South Carolina	Cherokee County	Cecil silt loam	6.6	2	1	52	55	48	7
Texas	San Marcos	Houston black clay	7.9	8	8	21	37	30	7
Alabama	King's farm	Orangeburg clay	10.3	3	6	17	26	19	7
South Carolina	York County	Iredell clay loam	7.7	0	6	19	25	18	7
Wisconsin	Portage County	Marshall gravelly loam.	11.0	−1	−2	14	11	4	7
Alabama	Lee County	Norfolk coarse sand.	5.3	−7	15	48	56	50	6
Arkansas	Prairie County	Acadia silt loam	11.2	0	4	29	33	27	6

TABLE IV.—*Percentage increase in growth attributable to P, K, and N, and the sum of the same, etc.*—Continued.

State.	Locality.	Soil.	Weight of plants on untreated soil.	Increase attributable to—			Sum of P, K, and N.	Increase attributable to PKN.	Difference.
				P.	K.	N.			
			Grams.	*P.ct.*	*P.ct.*	*P.ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Arkansas	Prairie County	Morse clay	10.8	4	−3	2	3	−3	6
Georgia	Waycross area	Norfolk sand	6.1	−2	−5	36	29	24	5
Texas	Rusk County	Orangeburg fine sand.	7.5	−7	20	31	44	40	4
Virginia	Hanover County	Norfolk sandy loam.	7.5	3	11	20	34	30	4
Georgia	Waycross area	Norfolk fine sand	6.1	7	15	55	77	74	3
Arkansas	Prairie County	Acadia silt loam	7.3	1	7	10	18	15	3
Pennsylvania	Montgomery County.	Hagerstown loam.	10.3	13	−2	1	12	9	3
Tennessee	Henderson County.	Lexington silt loam.	7.5	1	1	36	38	36	2
North Carolina	Asheville	Porters clay	5.8	−6	−2	29	21	19	2
Texas	San Marcos area	Houston black clay	8.9	0	4	15	19	17	2
Missouri	Crawford County.	Clarksville stony loam.	14.6	4	3	−2	5	3	2
Texas	Maroney's farm	Orangeburg clay	8.6	−3	1	17	15	14	1
New York	Tompkins County	Dunkirk loam	8.4	−4	2	15	13	12	1
Indiana	Tippecanoe County.	Marshall loam	7.5	−3	2	7	6	6	0
Arkansas	Prairie County	Morse clay	8.8	−9	8	1	0	0	0
Arkansas	Prairie County	Crowley silt loam	10.1	−1	3	0	2	3	1
Indiana	Tippecanoe County.	Marshall silt loam.	7.2	4	1	6	11	12	1
Arkansas	Prairie County	Acadia silt loam	9.0	0	11	6	17	18	1
North Carolina.	New Hanover County.	Norfolk fine sandy loam.	7.3	3	3	22	28	29	1
New York	Tompkins County	Dunkirk clay loam	4.5	−18	4	55	41	42	1
Ohio	Westerville area	Miami loam	8.6	−8	3	−2	−7	−5	2
Arkansas	Prairie County.	Waverly silt loam.	7.8	−7	9	−7	−5	−3	2
South Carolina.	Cherokee County	Cecil fine sandy loam.	5.9	−3	7	46	50	52	2
North Carolina.	Statesville	Cecil clay (good)	8.8	0	−2	−4	−6	−4	2
Texas	Galveston	Galveston clay	11.2	−14	−12	3	−23	−20	3
Texas	Rusk County	Susquehanna fine sandy loam.	7.0	−3	0	9	6	9	3
Texas	Rusk County	Norfolk fine sand	7.8	−4	8	21	25	28	3
Kentucky	McCracken County.	Memphis silt loam.	5.0	−3	3	39	39	42	3
Alabama	Lee County	Norfolk sand	6.8	9	10	40	59	62	3
Iowa	Leon	Kansan till	5.9	7	15	48	70	73	3
Louisiana	Caddo Parish	Caddo fine sandy loam.	8.8	−7	5	7	5	9	4
Texas	San Antonio	Houston black clay loam.	5.8	8	1	−3	6	10	4
North Carolina.	Statesville	Cecil clay (poor)	8.8	−1	1	0	0	5	5
New York	Tompkins County.	Miami stony loam.	9.6	4	1	1	6	11	5
Georgia	Waycross	Norfolk sandy loam.	6.5	11	15	54	80	85	5
Arkansas	Prairie County	Crowley silt loam	7.1	−8	0	9	1	7	6
Maryland	Leonardtown	Leonardtown loam (poor).	6.5	−7	15	8	16	22	6
Texas	Rusk County	Norfolk fine sand	8.6	5	6	19	30	36	6
Alabama	Rawles's farm	Orangeburg sandy loam.	8.1	6	−5	4	5	12	7
Texas	San Marcos area	Houston black clay	8.1	−4	−5	21	12	19	7
Alabama	Lee County	Norfolk sand	4.7	−1	−1	30	28	35	7
South Carolina.	Cherokee County.	Cecil sandy loam	6.9	−12	28	35	51	58	7
Mississippi	Montgomery County.	Memphis silt loam.	8.6	−13	6	12	5	13	8
Louisiana	Caddo Parish	Orangeburg fine sandy loam.	6.5	3	3	0	6	15	9
Texas	San Marcos area	Crawford silt clay.	9.2	−7	2	19	14	23	9
South Carolina.	Cherokee County.	Cecil clay	7.4	−4	−6	36	26	35	9
Virginia	Pocahontas field	Cecil clay	11.7	−3	4	−3	−2	9	11
Mississippi	Pontotoc County.	Monroe silt loam	8.0	−4	−6	13	3	14	11
New York	Binghamton area.	Wabash loam	10.6	−1	11	5	15	26	11
Missouri	Crawford County.	Wabash silt loam	7.6	−11	1	−3	−13	−1	12
Georgia	Waycross	Norfolk sand	5.5	−9	24	45	60	72	12
South Carolina.	St. Matthews	Orangeburg sandy loam.	11.8	0	−2	15	13	26	13
Texas	Palestine	Orangeburg fine sandy loam.	11.4	−7	−4	11	0	14	14

TABLE IV.—*Percentage increase in growth attributable to P, K, and N, and the sum of the same, etc.*—Continued.

State.	Area.	Soil.	Weight of plants on untreated soil.	Increase attributable to—			Sum of P, K, and N.	Increase attributable to PKN.	Difference.
				P.	K.	N.			
			Grams.	*P.ct.*	*P.ct.*	*P.ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Pennsylvania	Montgomery County.	Chester loam	7.8	0	9	4	13	27	14
North Carolina.	Union County	Silt loam	4.6	− 4	0	32	28	42	14
Alabama	Lee County	Norfolk sandy loam.	6.1	−14	4	42	32	46	14
North Carolina.	New Hanover County.	Norfolk fine sand	6.4	3	9	37	49	63	14
Ohio	Westerville area	Miami black clay loam.	8.3	−11	6	− 2	− 7	8	15
Florida	Escambia County	Norfolk fine sandy loam.	5.5	10	12	− 5	17	32	15
Illinois		Marion silt loam	7.7	−13	− 8	− 3	−24	− 8	16
Louisiana	Caddo Parish	Orangeburg fine sandy loam.	5.0	0	6	10	16	32	16
Wisconsin	Portage County	Portage silt loam	8.7	2	−16	− 2	−16	1	17
Alabama	Lee County	Norfolk coarse sand.	6.4	−12	0	20	8	25	17
Iowa		Wisconsin drift (good).	9.6	−10	15	30	35	52	17
Georgia	Waycross	Portsmouth fine sand.	5.5	2	18	33	53	71	18
Mississippi	Montgomery County.	Memphis silt loam.	10.6	−13	− 3	− 2	−18	1	19
Indiana	Newton County	Clyde fine sand	12.6	−21	− 2	−14	−37	−17	20
Mississippi	Montgomery County.	Memphis silt loam.	9.5	−16	− 9	0	−25	− 5	20
New Jersey	Woodbine	Norfolk fine sandy loam.	6.5	1	1	9	11	32	21
Georgia	Waycross	Norfolk sandy loam.	7.0	− 7	14	36	43	64	21
Virginia	Hanover County	Wickham sandy loam.	7.5	− 3	5	11	13	36	23
Alabama	Marion	Orangeburg sandy loam.	4.8	14	7	25	46	69	23
Georgia	Waycross	Portsmouth fine sand.	5.2	1	15	50	66	90	24
North Carolina.	Chowan County	Portsmouth silt loam.	4.5	2	19	14	35	62	27
Wisconsin	Portage County	Portage silt loam	10.0	−11	− 9	− 6	−26	3	29
Mississippi	Montgomery County.	Memphis silt loam.	10.2	− 3	− 2	−15	−20	12	32
Alabama	Lee County	Cecil sandy loam	5.6	−11	− 7	29	11	43	32
Mississippi	Pontotoc County.	Orangeburg clay	6.6	− 9	3	18	12	45	33
Georgia	Waycross	Norfolk fine sand	7.4	− 9	− 8	− 3	−20	14	34
Mississippi	Montgomery County.	Memphis silt loam.	11.2	−10	− 7	−11	−28	8	36
Texas	Rusk County	Orangeburg fine sandy loam.	9.2	−12	− 6	14	− 4	36	40
Louisiana	Caddo Parish	Norfolk fine sandy loam.	7.9	1	− 5	−10	−14	35	49
Indiana	Newton County	Muck	4.4	−25	61	14	50	100	50
South Carolina.	York County	Cecil sand	3.9	−15	− 8	26	3	54	51
Louisiana	Caddo Parish	Orangeburg fine sand.	5.0	−22	−10	−10	−42	28	70
Rhode Island	Kingston	Miami silt loam	3.6	− 8	−19	−14	−41	31	72

TABLE V.—*Average percentage increase in growth attributable to P, K, and N and the aggregate increase of the same salts used individually as compared with the actual increase when the same salts were used together, averages being for the soils in which the difference between the aggregate and actual increase is within limits indicated in the first column.*

Range of difference.	Number of soils.	Green weight of plants.	Increase attributable to—			Sum of P, K, and N.	Increase attributable to mixture of PKN.	Difference.
			P.	K.	N.			
Per cent.		*Grams.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
60+	5	4.8	37	49	64	150	52	98
50–59	8	7.0	31	31	38	100	46	54
40–49	7	6.4	19	30	35	84	41	43
30–39	16	6.7	16	22	31	69	34	35
20–29	19	7.3	13	19	38	70	46	24
10–19	35	7.6	6	12	22	40	26	14
0–9	28	8.3	1	5	22	28	23	5
9–0	32	7.6	−2	4	17	19	23	−4
19–10	20	7.9	−5	4	14	13	28	−15
29–20	9	7.5	−4	4	14	14	37	−23
39–30	5	8.2	−8	−5	4	−9	24	−33
49–40	2	8.6	−6	−5	2	−9	36	−45
50+	4	4.2	−18	6	4	−8	53	−61

TABLE VI.—*Ten soils in which percentage increase attributable to each ingredient is greater than that produced when all are combined.*

State.	Locality.	Soil type.	Weight of plants grown on untreated soil.	Increase attributable to—			Sum of PKN.	Increase attributable to mixture of PKN.	Difference.
				P.	K.	N.			
			Grams.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Louisiana	Caddo Parish	Miller fine sand	7.3	21	26	10	57	1	56
Iowa	Ames	Peat	15.0	24	26	21	71	20	51
Missouri	Crawford County	Clarksville silt loam.	6.6	26	15	17	58	7	51
Indiana	Newton County	Marshall loam	7.6	17	22	17	56	16	40
Florida	Escambia County	Norfolk sand	5.4	16	18	13	47	11	36
New York	Geneseo	Dunkirk clay loam.	10.2	11	11	18	40	5	35
Indiana	Newton County	Marshall fine sandy loam.	6.3	5	12	9	26	−4	30
Arkansas	Prairie County	Morse clay	11.1	5	13	−3	15	−11	26
Arkansas	Prairie County	Crowley silt loam.	8.1	9	14	2	25	0	25
New York	Binghamton area.	Dunkirk gravelly sandy loam.	6.6	4	1	11	16	1	15
	Average		8.4	14	16	11	41	5	36

TABLE VII.—*Ten soils in which two of the three ingredients each produced a greater increase than when all three were combined.*

State.	Locality.	Soil type.	Weight of plants grown on untreated soil.	Increase attributable to—			Sum of PKN.	Increase attributable to mixture of PKN.	Difference.
				P.	K.	N.			
			Grams.	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*
Virginia	Portsmouth	Peat	3.2	53	112	69	234	69	165
Louisiana	Caddo Parish	Norfolk fine sand	3.7	−3	51	62	110	51	59
Louisiana	Caddo Parish	Caddo fine sandy loam.	6.0	6	17	26	49	8	41
Louisiana	Caddo Parish	Caddo fine sandy loam.	5.0	−10	4	33	27	4	23
Louisiana	Caddo Parish	Norfolk fine sandy loam.	9.6	−8	9	13	14	−1	15
New York	Binghamton area	Dunkirk gravelly loam.	10.6	9	9	1	19	7	12
Florida	Escambia County	Norfolk fine sandy loam.	8.4	−7	14	15	22	11	11
Wisconsin	Portage County	Miami sandy loam.	9.0	4	8	2	14	3	11
Arkansas	Prairie County	Morse clay	10.8	4	−3	2	3	−3	6
Missouri	Crawford County	Clarksville stony loam.	14.6	4	3	−2	5	3	2
	Average		8.1	5	23	22	50	15	35

NITRATE OF SODA ALONE AND WITH OTHER SALTS.

A study of Table IV shows that in 66 per cent of the instances nitrate of soda when used alone has produced an increase of growth which equals or exceeds that produced by either sulphate of potash or acid phosphate.

A tabulation of the data for nitrate of soda and of combinations in which it enters shows that the nitrate of soda has a marked beneficial effect on the majority of soils which on an average is not increased by the addition of acid phosphate. A comparison of the nitrate with the nitrate-phosphate column shows a difference in favor of the former in slightly more than half of the comparisons. The average of these two columns shows a difference of less than one-tenth of 1 per cent.

Nitrate of soda when supplemented with sulphate of potash gives an increase in growth which in 74 per cent of the instances equals or exceeds that produced by nitrate of soda alone, the average result being 8.5 per cent in favor of the combination. When this nitrogen-potash combination is still further supplemented by acid phosphate there is on an average no additional increase in growth. In fact the instances in which the nitrogen-potash combination equals or exceeds that of the complete fertilizer are slightly in the majority. The tabulation above mentioned is not published, but the same facts may be gathered by careful study of those columns in Table III, which give the results for nitrogen and all combinations into which it enters.

SULPHATE OF POTASH ALONE AND WITH OTHER SALTS.

Sulphate of potash when supplemented by acid phosphate produced an increase in growth, which in 50 per cent of the soils exceeded that produced by potash alone, the average increase being one-tenth of 1 per cent in favor of the combination. When the potash salt is combined with nitrate of soda there is a marked increase in growth over that produced by potash alone, which, on the average, is not further increased by the addition of acid phosphate. In 86 per cent of the soils the effect of potash combined with nitrogen has equaled or exceeded the effect of potash alone. These facts are brought out by a study of the columns in Table III, in which potash occurs, omitting all soils for which the data for this salt and all its combinations are incomplete.

ACID PHOSPHATE ALONE AND WITH OTHER SALTS.

Referring to Table IV, the striking fact is the large number of instances in which acid phosphate gives a small or negative effect. The efficiency is quite regularly increased (see all columns of Table III in which phosphate enters) as each fertilizer salt is added, the exceptions to this being mostly for those soils in which the efficiency of the complete fertilizer as a whole becomes quite small or is negative.

In the life and economy of the plant, phosphates are generally recognized to be instrumental chiefly in the production of seed or fruit, and have a tendency to hasten maturity, and may influence the color and quality of the fruit. It is also known that plants do not absorb extraneous phosphates during the very early stages of growth. From the standpoint of the requirements of the plant, no response would be expected from the phosphates, and it is, therefore, not strange that in many instances a small or negative effect has resulted from their application. It should be borne in mind, however, that this is not a study of the plant's requirements, but a study of the fertility of the soil as affected by fertilizers and that the plants have been used merely as the indicator of the degree to which fertility has been affected by the various applications. It is now contended that aside from the direct action that various salts have on the growth and economy of the plant, they may also act directly on the soil, thereby increasing its fertility in a way not fully understood.

An inspection of the tables will show that while small and negative effects have often resulted from the phosphate, there are 55 soils in which the increase in growth attributable to this salt when used alone has ranged from 10 to 50 per cent and in two instances even more.

LIME ALONE AND WITH FERTILIZER SALTS.

Table VIII shows the increase in growth attributable to lime, to a complete fertilizer with and without lime, to manure, and to cowpea vines with lime. The soils are arranged in a descending series as determined by the efficiency of the complete fertilizer without lime. Lime alone shows quite a marked effect in the majority of the soils, and while its efficiency corresponds in a general way with that of a complete fertilizer there are numerous exceptions to this. The lime may have little or no effect where the fertilizer is markedly beneficial. For example, in the upper portion of the table where the figures for the complete fertilizer range from 50 to 75 per cent increase in growth there are 8 soils on which lime gives less than 10 per cent increase, while in the lower portion of the table where the complete fertilizer does not exceed 11 per cent there are 7 instances where the increase in growth attributable to lime exceeds 30 per cent. As a rule, the efficiency of the complete fertilizer has been appreciably increased by the addition of lime. There seems to be little evidence in support of the contention sometimes made that the benefits due to lime are attributable to its favorable action on nitrification.

A study of Table IX, which summarizes the results of Table VIII and all data for the same soils in Table III—i. e., gives the mean percentage increase in growth attributable to the several fertilizer salts and combinations for groups of soils in which the efficiency of a complete fertilizer falls within certain limits as given in the second column—shows that as the efficiency of a complete fertilizer declines there is a corresponding decline in the effect of practically all ingredients and combinations. This is equally as true for manure or for potash and phosphate as it is for nitrate of soda and lime, so that the parallel decline in the lime and nitrate columns in the table loses significance. Of the soils in Table VIII, where the efficiency of a complete fertilizer is not less than 25 nor more than 75 per cent, there are 17 in which the efficiency of lime exceeds 35 per cent and 31 in which it is 10 per cent or less. As a result of averages of these two groups of soils, we get the following results: Seventeen soils (lime giving increase of 35 per cent or more) average efficiency, lime 63, N 35, NKP 49; 31 soils (lime giving increase of 10 per cent or less) lime 4, N 24, NKP 40. The effect of nitrogen is obtained from Table III.

The difference in the efficiency of lime is here very marked, dropping from an average of 63 per cent for the 17 soils to only 4 per cent for the 31 soils. The relative decline in the effect of nitrate of soda and the complete fertilizer, however, is small, being from 35 to 24 for the former and 49 to 40 for the latter.

TABLE VIII.—*Weight of plants on the untreated soil and the percentage increase in growth produced by lime, a complete fertilizer with lime, a complete fertilizer, manure, and cowpea vines with lime.*

State.	Locality.	Soil.	Weight of plants, untreated soil.	Increase attributable to—				
				L.	NPKL.	NPK.	M.	CvL.
			Grams.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
North Carolina	New Hanover County.	Norfolk sand	4.1	66	154	151	254	144
North Carolina	New Hanover County.	Portsmouth fine sand.	3.0	70	173	110	130	230
North Carolina	Iredell test farm	Cecil clay	4.5	45	105	105	90	......
Virginia	Louisa County	Cecil loam	4.6	71	153	102	63	158
Indiana	Newton County	Peat	4.4	14	70	100	40	18
Georgia	Waycross area	Portsmouth fine sand.	5.2	92	153	90	219	175
Georgia	Waycross area	Norfolk fine sandy loam.	3.9	64	105	86	150	176
Georgia	Waycross area	Norfolk sandy loam	6.5	35	100	85	109	109
Iowa	Ames	Wisconsin drift (poor).	7.7	17	....	82	86	......
Georgia	Waycross area	Portsmouth fine sand.	5.2	29	117	77	150	148
Georgia	Waycross area	Norfolk fine sand	6.1	34	84	74	102	107
Georgia	Waycross area	Norfolk fine sandy loam.	7.5	40	89	73	113	113
Iowa	Leon	Kansan till	5.9	6	42	73	24	......
Georgia	Waycross area	Norfolk sand	5.5	64	109	72	124	118
Georgia	Waycross area	Portsmouth fine sand.	5.5	20	75	71	64	109
Alabama	Marion	Orangeburg sandy loam.	4.8	12	69	69	37	60
Virginia	Portsmouth	Peat	3.2	75	97	69	47	72
Alabama	Marion	Orangeburg clay	9.1	20	55	67	49	35
Texas	Rusk County	Norfolk fine sandy loam.	7.5	21	64	65	105	62
Georgia	Waycross area	Norfolk sandy loam.	7.0	0	57	64	103	94
North Carolina	New Hanover County..	Norfolk fine sand	6.4	16	70	63	94	37
North Carolina	Tarboro	Norfolk fine sandy loam.	3.0	1	70	63	38	78
Alabama	Lee County	Norfolk sandy loam.	7.7	19	87	63	61	164
North Carolina	Chowan County	Portsmouth silt loam.	4.5	19	57	62	46	74
Alabama	Lee County	Norfolk sand	6.8	57	103	62	107	160
Louisiana	Caddo Parish	Norfolk fine sand	5.3	9	74	59	28	80
Indiana	Tippecanoe County.	Miami silt loam	5.6	17	35	58	71	30
South Carolina	Cherokee County	Cecil sandy loam	6.9	4	65	58	71	5
Georgia	Waycross area	Norfolk sand	5.6	20	121	57	114	132
Iowa	Blackhawk County.	Iowan drift	9.0	36	....	57	69	......
North Carolina	Edgecombe	Norfolk fine sandy loam.	4.8	25	77	56	66	......
North Carolina	Pinehurst	Portsmouth sand	4.8	26	46	56	41	45
Louisiana	Caddo Parish	Norfolk fine sand	5.4	39	80	56	92	98
South Carolina	York County	Cecil sand	3.9	8	51	54	90	60
South Carolina	Cherokee County	Cecil fine sandy loam.	5.9	29	68	52	88	123
Iowa	Ames	Wisconsin drift (good).	9.6	− 5	....	52	47	......
Louisiana	Caddo Parish	Norfolk fine sand	3.7	41	113	51	146	195
Alabama	Lee County	Norfolk coarse sand.	5.3	5	70	50	59	101
Mississippi	Pontotoc area	Lufkin silt loam	5.4	63	56	50	37	78
Georgia	Waycross area	Norfolk fine sand	6.0	27	32	50	113	107
North Carolina	Raleigh	Cecil sandy loam	4.1	52	103	49	53	54
Texas	Rusk County	Norfolk fine sand	8.5	21	55	49	86	48
South Carolina	Cherokee County	Cecil silt loam	6.6	39	56	48	81	74
Florida	Escambia County	Norfolk fine sandy loam.	3.3	136	130	48	90	136
Mississippi	Montgomery County.	Orangeburg fine sandy loam.	7.5	24	64	48	60	60
Texas	Rusk County	Norfolk fine sandy loam.	6.1	40	41	48	48	80
Texas	Rusk County	Caddo fine sandy loam.	8.2	7	47	47	61	57
Wisconsin	Portage County	Muck	7.2	23	41	47	51	16

TABLE VIII.—*Weight of plants on the untreated soil and the percentage increase in growth produced by lime, etc.*—Continued.

State.	Locality.	Soil.	Weight of plants, untreated soil.	Increase attributable to—				
				L.	NPKL.	NPK.	M.	CvL.
			Grams.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Florida	Escambia County	Norfolk sand	5.9	24	55	46	94	97
Alabama	Lee County	Norfolk sandy loam.	6.1	11	64	46	42	104
Mississippi	Pontotoc County.	Orangeburg clay	6.6	−3	47	45	18	32
Alabama	Lee County	Cecil sandy loam	5.6	13	52	43	43	...
New York	Tompkins County.	Dunkirk clay loam.	4.5	29	....	42	33	54
North Carolina	Union County	Silt loam	4.6	4	51	42	28	.....
Kentucky	McCracken County.	Memphis silt loam.	5.0	18	48	42	70	2
Texas	San Marcos area	Crawford silt clay	8.8	24	46	42	56	11
Arkansas	Prairie County	Acadia silt loam	7.4	23	48	41	31	38
Texas	Rusk County	Orangeburg fine sand.	7.5	8	60	40	80	68
Wisconsin	Portage County	Miami sand	6.0	7	43	39	80	−4
Arkansas	Prairie County	Waverly silt loam	6.5	61	55	38	38	54
Virginia	Louisa County	Wickham sandy loam.	7.5	9	35	36	31	−12
Tennessee	Henderson County.	Lexington silt loam.	7.5	5	57	36	72	17
Louisiana	Caddo Parish	Caddo fine sandy loam.	4.4	18	52	36	20	186
Texas	Rusk County	Norfolk fine sand	8.6	10	26	36	61	37
Texas	Rusk County	Orangeburg fine sandy loam.	9.2	13	39	36	68	53
Wisconsin	Portage County	Marshall sand	8.4	11	8	35	34	3
New York	....	Volusia silt loam	4.8	15	62	35	81	...
South Carolina	Cherokee County.	Cecil clay	7.4	4	44	35	42	12
Alabama	Lee County	Norfolk sand	4.7	50	135	35	108	143
Louisiana	Caddo Parish	Norfolk fine sandy loam.	7.9	2	56	35	18	47
Texas	San Marcos area	Houston black clay.	7.0	17	42	35	10	38
North Carolina	Statesville	Iredell clay loam	5.2	−1	28	34	33	...
South Carolina	York County	Cecil sandy loam	7.0	33	41	34	76	58
Texas	Rusk County	Caddo fine sandy loam.	8.1	17	36	34	62	40
Louisiana	Caddo Parish	Norfolk fine sandy loam.	5.6	28	54	33	54	52
Texas	San Marcos area	Blanco loam	8.7	20	21	33	28	37
Florida	Escambia County.	Norfolk fine sandy loam.	5.5	45	82	32	32	85
Louisiana	Caddo Parish	Orangeburg fine sandy loam.	5.0	0	44	32	34	96
New Jersey	Woodbine	Norfolk fine sandy loam.	6.5	7	31	32	28	42
Rhode Island	Kingston	Miami silt loam	3.6	133	111	31	39	...
Virginia	Louisa County	Cecil sandy loam	7.2	5	39	30	25	57
Virginia	Hanover County	Norfolk sandy loam	7.5	−1	47	30	44	−8
North Carolina	Wake County	Tobacco soil	4.7	11	16	30	.....	...
Texas	San Marcos area	Houston black clay.	7.9	15	21	30	30	42
North Carolina	New Hanover County.	Norfolk fine sandy loam.	7.3	8	31	29	57	34
Missouri	Scotland County	Shelby silt loam	9.6	11	28	28	60	30
New York	Geneseo	Dunkirk clay loam	8.9	19	22	28	17	28
Mississippi	Pontotoc area	Lufkin clay	6.4	6	31	28	9	48
Louisiana	Caddo Parish	Orangeburg fine sand.	5.0	12	15	28	114	124
Arkansas	Prairie County	Waverly silt loam	5.0	104	150	28	10	132
Texas	Rusk County	Norfolk fine sand	7.8	3	60	28	103	69
Pennsylvania	Montgomery County.	Chester loam	7.8	4	33	27	13	8
South Carolina	Cherokee County.	Iredell clay loam	9.1	14	42	27	36	7
Arkansas	Prairie County	Crowley silt loam	7.0	43	71	27	64	80
Arkansas	Prairie County	Acadia silt loam	11.2	12	33	27	46	27
South Carolina	St. Matthews	Orangeburg sandy loam.	11.8	19	28	26	25	17
New York	Binghamton County.	Wabash loam	10.6	10	15	26	31	10
Mississippi	Pontotoc County.	Orangeburg sandy loam.	7.6	6	39	26	25	24
Arkansas	Prairie County	Calhoun clay	8.3	18	27	26	4	13
Texas	Rusk County	Orangeburg fine sandy loam.	9.2	12	37	26	37	60
North Carolina	Biltmore	Porters clay	12.4	31	26	25	61	24

TABLE VIII.—*Weight of plants on the untreated soil and the percentage increase in growth produced by lime, etc.*—Continued.

State.	Locality.	Soil.	Weight of plants, untreated soil.	Increase attributable to—				
				L.	NPKL.	NPK.	M.	CvL.
			Grams.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Georgia	Waycross area	Norfolk sandy loam	5.0	− 9	43	25	54	42
Alabama	Lee County	Norfolk coarse sand	6.4	22	23	25	33	41
Illinois	Manito	Muck	9.4	7	33	25	45	51
North Carolina	Blantyre	Porters sandy loam.	4.5	43	22	24	61	31
Georgia	Waycross area	Norfolk sand	6.1	34	55	24	77	65
Georgia	Waycross area	Norfolk fine sandy loam.	7.9	22	35	24	96	67
Texas	Nacogdoches	Orangeburg fine sandy loam.	8.8	16	24	24	56	15
New York		Volusia silt loam	6.6	8	15	23	77	13
Texas	San Marcos area	Crawford silt clay	9.2	4	31	23	14	34
Wisconsin	Portage County	Miami stony sand	9.9	− 3	19	22	47	8
Florida	Escambia County	Norfolk sand	7.2	29	23	22	66	65
Mississippi	Montgomery County.	Lintonia loam	8.5	24	16	22	30	48
Texas	San Marcos area	Crawford silt clay	9.2	20	42	22	40	52
Illinois	Pulaski County	Red silt loam	7.0	16	38	22	26	45
Louisiana	Caddo Parish	Orangeburg fine sand.	7.4	20	28	21	15	28
New York	Ithaca	Volusia silt loam	5.4	9	32	20	51	29
New Jersey	Woodbine	Norfolk sandy loam	6.0	2	17	20	25	14
Iowa	Ames	Muck	15.0	−14	......	20	64	......
North Carolina	Asheville	Porters clay	5.8	10	53	19	9	16
Alabama	Perry County	Orangeburg clay	10.3	16	35	19	32	26
Louisiana	Caddo Parish	Miller fine sand	5.8	22	34	19	81	48
Texas	San Marcos area	Houston black clay.	8.1	6	26	19	25	32
South Carolina	York County	Iredell clay loam	7.7	3	17	18	51	19
Arkansas	Prairie County	Acadia silt loam	9.0	−11	41	18	32	21
Texas	San Marcos area	Houston black clay.	8.9	5	23	17	8	23
Indiana	Newton County	Marshall loam	7.6	22	21	16	77	34
Alabama	Lee County	Cecil sandy loam	8.6	10	28	15	....	58
Louisiana	Caddo Parish	Orangeburg fine sandy loam.	6.5	7	15	15	20	26
Arkansas	Prairie County	Acadia silt loam	7.3	14	37	15	7	16
Georgia	Waycross area	Norfolk fine sand	7.4	6	25	14	28	36
Mississippi	Pontotoc County.	Monroe silt loam	8.0	9	18	14	29	39
Texas	Nacogdoches	Orangeburg clay	8.6	4	5	14	29	5
Texas	Palestine	Orangeburg fine sandy loam.	11.4	−15	9	14	37	43
Mississippi	Montgomery County.	Memphis silt loam	7.0	13	17	14	36	40
Ohio	Westville area	Miami clay loam	6.1	7	11	13	15	45
Pennsylvania	Montgomery County.	Penn silt loam	12.3	− 8	4	13	24	36
Mississippi	Montgomery County.	Memphis silt loam	8.6	6	9	13	6	34
Indiana	Tippecanoe County.	Marshall silt loam	7.2	− 7	6	12	−2	4
New York	Tompkins County	Dunkirk loam	8.4	− 7	11	12	46	0
Alabama	Perry County	Orangeburg sandy loam.	8.1	21	17	12	17	20
Mississippi	Montgomery County.	Memphis silt loam	10.2	1	20	12	18	28
New York	Tompkins County	Dunkirk clay loam	9.0	−14	12	11	68	− 5
New York	Tompkins County	Miami stony loam	9.6	0	7	11	36	26
Florida	Escambia County	Portsmouth sand	8.3	48	48	11	47	35
Florida	Escambia County	Norfolk sand	5.4	46	74	11	83	107
Florida	Escambia County	Norfolk fine sandy loam.	8.4	35	14	11	32	51
Texas	San Antonio	Houston black clay loam.	5.8	11	10	10	19	− 7
Pennsylvania	Montgomery County.	Hagerstown loam	10.3	6	23	9	20	29
Louisiana	Caddo Parish	Caddo fine sandy loam.	8.8	8	14	9	6	41
Louisiana	Caddo Parish	Norfolk fine sandy loam.	8.7	0	30	9	9	25
Texas	Rusk County	Susquehanna fine sandy loam.	7.0	−11	26	9	29	56
Ohio	Westerville area	Miami black clay loam.	8.3	1	11	8	22	5
Mississippi	Montgomery County.	Memphis silt loam	11.2	0	−3	8	5	9

TABLE VIII.—*Weight of plants on the untreated soil and the percentage increase in growth produced by lime, etc.*—Continued.

State.	Locality.	Soil.	Weight of plants, untreated soil.	Increase attributable to—				
				L.	NPKL.	NPK.	M.	Cvl.
			Grams.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Louisiana	Caddo Parish	Caddo fine sandy loam.	6.0	19	16	8	79	23
Missouri	Crawford County	Clarksville silt loam	6.6	14	1	7	43	32
Pennsylvania	Montgomery County.	Lansdale silt loam	9.9	19	17	7	9	30
New York	Binghamton area.	Dunkirk gravelly loam.	10.6	−3	−11	7	20	−9
Arkansas	Prairie County	Crowley silt loam	7.1	36	60	7	19	38
Indiana	Tippecanoe County.	Marshall loam	7.5	−3	7	6	42	−2
New York	Geneseo	Dunkirk clay loam	10.2	8	0	5	17	21
Wisconsin	Portage County	Marshall gravelly loam.	11.0	2	3	4	36	14
Louisiana	Caddo Parish	Caddo fine sandy loam.	5.0	8	72	4	44	148
Wisconsin	Portage County	Miami sandy loam	9.0	4	21	3	29	12
Wisconsin	Portage County	Portage silt loam	10.0	5	10	3	21	10
Missouri	Crawford County	Clarksville stony loam.	14.6	−3	−2	3	−10	13
Arkansas	Prairie County	Crowley silt loam.	10.1	2	5	3	7	9
Wisconsin	Portage County	Portage silt loam.	8.7	9	−14	1	42	−14
New York	Binghamton area.	Dunkirk gravelly sandy loam.	6.6	26	27	1	29	69
Mississippi	Montgomery Co.	Memphis silt loam	10.6	−1	16	1	−4	6
Louisiana	Caddo Parish	Miller fine sand	7.3	14	16	1	43	36
Arkansas	Prairie County	Crowley silt loam	8.1	46	33	0	18	42
Arkansas	Prairie County	Morse clay	8.8	6	−7	0	6	22
Missouri	Crawford County	Wabash silt loam	7.6	0	2	−1	23	24
Louisiana	Caddo Parish	Norfolk fine sandy loam.	9.6	6	19	−1	22	1
Arkansas	Prairie County	Morse clay	10.8	2	4	−3	4	9
Arkansas	Prairie County	Waverly silt loam	7.8	37	40	−3	18	41
Indiana	Newton County	Marshall fine sandy loam.	6.3	−12	−1	−4	60	−2
North Carolina	Statesville	Cecil clay (good)	8.8	5		−4	9	
Ohio	Westerville area	Miami loam	8.6	2	2	−5	48	15
Mississippi	Montgomery County.	Memphis silt loam.	9.5	−5	3	−5	−5	11
Ohio	Strongsville	Miami clay loam		30		−6	9	
Illinois	Clinton County	Marion silt loam	7.7	−13	−4	−8	48	−12
Arkansas	Prairie County	Morse clay	11.1	−7	−1	−11	5	4
Indiana	Newton County	Clyde fine sand	12.6	−12	−7	−17	32	−4
Texas	Galveston	Galveston clay	11.2	−2	−8	−20	4	31

RELATIVE EFFICIENCY OF ORGANIC AND CHEMICAL MANURES.

An examination of Table VIII shows further the efficiency of manure and cowpea vines with lime as compared with a complete fertilizer with and without lime. In the majority of instances the manure or cowpea vines with lime, or both, have proved superior to the mineral fertilizers. A careful analysis of the results shows that manure and cowpea vines with lime nearly tie for first rank, while the complete fertilizer with lime ranks third, and without lime becomes fourth, or last. The relative number of times that each treatment ranks first on the basis of 100 for the whole is: Manure, 39; cowpea vines with lime, 39; complete fertilizer with lime, 16, and complete fertilizer alone, 6.

RELATIVE EFFICIENCY OF ALL SALTS AND COMBINATIONS WHEN SOILS ARE GROUPED ACCORDING TO EFFICIENCY OF PKN.

Table IX is an aggregation of the results in Table VIII and the results for the same soils in Table III and gives the average percentage increase in growth attributable to each ingredient and combination of ingredients for groups of soils in which the efficiency of a combination of nitrate, potash, and phosphate was within certain limits as given in the second column of the table. It also gives the average green weight of plants grown on the untreated soil for each of the groups as well as the weight produced by a complete fertilizer and the weight produced by the best average treatment for each group which in eight instances is attributable to cowpea vines with lime and in three instances to manure.

The efficiency of the single fertilizers, phosphate, potash, lime and nitrate, with a few exceptions increase in the order named, the phosphate being least effective and the nitrate most effective. In the group of soils for which the efficiency of a complete fertilizer is 60 to 69 per cent, potash outranks lime by 1 per cent, and in the following group it becomes identical with lime. In the last two groups in the table lime outranks the nitrate as well as potash and phosphate. A comparison of the efficiency of the several combinations of fertilizer salts and lime gives the order of efficiency that would be expected from a study of the relative efficiency of the same salts used separately. With a few exceptions, however, the efficiency of the various combinations is a little less than the aggregate efficiency of the same salts when used separately. These exceptions are mostly with the combination of potash and nitrate (KN), which in six out of eleven groups gives a larger percentage increase in growth than the aggregate of the same ingredients used separately. The efficiency order of the combinations, beginning with the smallest, is phosphate-potash (PK), phosphate-nitrate (PN), potash-nitrate (KN), phosphate-potash-nitrate (PKN), and phosphate-potash-nitrate-lime (PKNL). In the four lowest groups of the table, however, the potash-nitrate (KN) combination outranks the complete fertilizer without lime. A comparison of the most efficient fertilizer treatment, viz, that of the three fertilizing salts and lime, with the results obtained with manure and with cowpea vines and lime shows only four groups in which the fertilizer with lime outranks the manure and no instances in which the cowpea vines with lime have failed to outrank the fertilizer with lime. Of the eleven groups, cowpea vines with lime rank first eight times and manure three times.

In the last three columns is given the average green weight of plants on the untreated soil, with a complete fertilizer, and with the best average treatment, for each of the eleven groups of soil. It is oticeable that as there is a regular decrease in the efficiency of the ertilizers there is a corresponding regular increase in the weight f plants produced on the untreated soil. In other words, the lower he producing capacity of the soils the greater their response to fer- ilizers. The decrease in the efficiency of a complete fertilizer with- ut lime is nearly inversely proportional to the increase in the weight f plants so that the weight of plants produced by the same fertilizer or any group of soils approaches a constant. The same is essentially rue for the best average treatment with a tendency toward the argest plants on the poorer soils, as shown by the maximum weights f plants for the second and third groups from the top of the table nder heading of best treatment.

TABLE IX.—*Average effect of fertilizer salts and combinations by groups according to the efficiency of PKN, also average weight of plants on untreated soil, average weight when treated with PKN, and average weight with best fertilizer treatment.*

Number of soils.	Range of efficiency.	Increase attributable to—											Weight of plants.		
		P.	K.	N.	L.	PK.	PN.	KN.	PKN.	LPKN.	Manure.	Cowpea vines and lime.	Untreated soil.	PKN.	Best treatment.
		P.ct.	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*Gms.*	*Gms.*	*Gms.*
5	100+	29	43	66	53	58	75	85	113	131	115	137	4.1	8.7	9.7
4	80–99	10	23	58	52	26	63	85	86	119	141	153	5.8	10.8	14.7
6	70–79	5	20	53	32	23	57	72	73	86	96	119	5.9	10.2	12.9
10	60–69	15	26	40	25	27	50	55	65	73	69	84	6.0	9.9	11.0
15	50–59	11	23	43	23	20	40	48	54	68	69	83	5.8	8.9	10.6
18	40–49	7	15	37	27	18	32	40	45	59	57	62	6.3	9.1	10.2
26	30–39	7	8	23	20	13	21	33	34	48	46	56	6.6	8.8	10.3
35	20–29	5	12	21	17	10	17	27	25	35	45	41	8.0	10.0	11.9
29	10–19	2	4	11	9	4	11	16	14	23	31	29	8.2	9.3	10.7
25	0– 9	1	5	6	8	2	6	12	5	15	24	26	9.0	9.5	11.3
13	−1 to −20	−7	0	0	2	−7	2	7	−7	4	21	11	9.3	8.7	11.2

RELATIVE EFFICIENCY OF SALTS WHEN USED ALONE AND IN COMBINATION.

In these tests as shown in Table III, beginning on page 15, each of the three salts, acid phosphate, sulphate of potash, and nitrate of soda, has been used separately and in three combinations, thus giving four observations relative to the increase in growth produced by each. For lime there are two observations, while for manure and cowpea vines and lime there is only one observation each. While it is disputed ground as to whether the efficiency of a fertilizer salt should be measured by using it alone or by combining it with all other elements in which the soil may be deficient, many experimenters have adopted the combination as the most reliable means. It seems probable, however, that theoretical considerations, rather than observed results, have led to the adoption of such a system, the idea being that if the soil is deficient in two or more ingredients the full benefits of any one of them can not be obtained in the absence of a sufficiency of the others. While such reasoning seems logical it is not always supported by facts, as may be seen by a study of Table IV. Here there are only 20 soils out of 190 in which this seems to be noticeably true, while there is a much larger number, viz, 50 soils, in which the efficiency of the ingredients used separately is much more marked than when used in combination, and this in spite of the fact that all three of them produce quite marked results. Indeed, when we calculate the average efficiency of the ingredients for all soils we find that each is slightly more efficient when used alone than when in combination with one or more other ingredients.

As an average of many field tests on various crops and in numerous localities the conclusion is that the efficiency of a fertilizer ingredient is about equally as marked whether used alone or in combination with one or more other ingredients. On the less productive soils the tendency is toward a better effect from the ingredient when in combination with other ingredients which are also beneficial. On better soils the tendency is in the other direction.[a] For many individual soils this tendency is as marked under field conditions as it is in the pots.

Numerous bulletins of the Alabama agricultural experiment station report the results of fertilizer tests that were conducted at intervals during the years 1889 to 1900. Of such tests 156 were cooperative experiments with cotton and were carried on in 53 of the 67 counties of the State. The fertilizer materials used per acre consisted of nitrogen derived from 90 pounds of sulphate of ammonia or 96 pounds of nitrate of soda or 200 pounds of cotton-seed meal, potash derived from 150 or 200 pounds of kainit or 64 pounds of muriate of potash, and phosphorus derived from 195 or 200 pounds of dissolved boneblack or 240 pounds of acid phosphate. The three classes of fertilizer were used separately and the three were also combined, each ingredient entering into the combination in the same amount as when used alone. The results are reported in pounds of seed cotton per acre over and above that produced when no fertilizer was used, and the data for each of the three fertilizers when used alone and in combination are complete for 134 tests. The aggregate increase attributed to the three fertilizers when used separately was 443.2 pounds of seed cotton per acre, as compared with an average of 444.7 pounds increase per acre when the same ingredients were combined.

Table X shows the percentage increase in growth attributable to each ingredient when used separately, as compared with the calculated increase where it occurs in the several combinations. The results are for each of the four ingredients, lime, nitrate, potash, and phosphate, and are the averages for each of the 25 areas given in Table III. As an illustration of how the results are calculated, take the average results of the five soils from Cherokee County, S. C. Nitrate alone gave an increase of 40 per cent. Nitrate and phosphate produced an increase of 36 per cent, or 40 per cent more than phosphate alone, while nitrate and potash produced 49 per cent, or 42 per cent more than potash alone. The average effect for nitrogen in these two combinations is therefore 41 per cent and is entered in the second column under nitrogen. As NP=36 and NK=49, by addition (2N)PK=85. However, PK=3, so by difference we have 2N=82 or N=41, which is entered in the third column under nitrogen. NPK=44 and since PK=3, N in the NPK combination produced an increase of 41 per cent. The four values each for potash and phosphate and the two values for lime are obtained in the same manner. For this area the efficiency of the several ingredients is very uniform, the range of variation for nitrate, potash, and phosphate being only 1 per cent, while for lime the difference between the two observations is 7 per cent. Since the results in Table X are based upon the average of all soils from each area the variation in the efficiency of the ingredients as they occur in the various combinations is not marked. By making the same calculations for each of the soils, however, many of them show a marked variation in the efficiency of the ingredients as they occur in the several combinations, a difference far too great to be attributable to error of observation, which by actual test has been found not to exceed plus or minus 5 per cent. Where the variation in the efficiency of a fertilizer ingredient, as it occurs alone and in several combinations, exceeds the limit of error in observations as above stated, such portion of the variation as exceeds that limit must be attributable to its association with the other ingredients. Just as in a solution of several salts the presence of one may increase or decrease the solubility of others, so in the soil the addition of one ingredient may increase or decrease the effectiveness of another. It has already been shown that for quite a number of soils the effect of three ingredients combined is no better than for one of them and that one ingredient may be substituted for another with equally good effect. See Table VI, page 30. On the other hand, there are many soils in which the effect attributable to a combination of three fertilizer ingredients is two or three times greater than the aggregate effect of the same ingredients when used separately. See latter portion of Table IV, page 26.

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[a] See tabulated results on corn in "Results in Field Experiments with Various Fertilizers," by Prof. W. O. Atwater, Ph. D., U. S. Dept. Agr., 1883.

The variation in the efficiency of a fertilizer ingredient as used separately and in several combinations bears no consistent relation to the efficiency of the ingredients with which it is associated or to the efficiency of the combination as a whole. If nitrate of soda produces an increase in growth which equals or exceeds that produced when it is associated with potash and phosphate, as is frequently shown in Table IV, page 26, we would theoretically expect little or no effect from either potash or phosphate when used alone on the same soils. Contrary to this theory, however, we find that, with an occasional exception, both potash and phosphate are markedly efficient on these soils. On the other hand, if nitrate of soda produces little or no increase as compared with a fair to good increase obtained when it is combined with potash and phosphate, as is frequently shown in the latter portion of Table IV, we should expect to obtain fair to good results from potash or phosphate when used alone on the same soils. But what do we find? Usually little or no effect from potash, and a negative effect from the phosphate. Table V, page 30, which is a condensation of the results in Table IV, shows up this relationship in a striking manner. In that table is given the average percentage increase in growth attributable to each of three ingredients and their combination for groups of soils in which the aggregate effect of the ingredients differs within certain limits from that obtained when they are used in combination. It will be noticed that there is a more or less regular and parallel decline in the efficiency of each of the ingredients when used separately, from a maximum of 37, 49, and 64 per cent for phosphate, potash, and nitrate to a minimum of – 18, – 5, and 2 for the same ingredients, respectively. Notwithstanding this marked decline in the efficiency of the ingredients when used separately, the efficiency for the three ingredients combined is essentially as marked at the end of the series as at the beginning, the average effect for the first and last groups being 52 and 53 per cent, respectively. The aggregate effect of the three ingredients used separately is 150 and – 8 per cent for the same groups. (See Table V, p. 30.)

TABLE X. *Percentage increase in growth attributable to each fertilizer salt and lime, when used alone and when used in various combinations, as calculated by the difference method. Average, by areas.*

State.	Locality.	Increase with lime.		Increase with phosphoric acid.			
		L. alone.	PKNL – PKN.	P. alone.	$\frac{(PK-K)+(PN-N)}{2}$	$\frac{PK+PN-KN}{2}$	PKN – KN.
		P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Indiana	Newton County	– 1	6	0	– 6	– 6	– 17
Missouri	Crawford County	4	– 3	6	2½	4	– 4
Ohio	Westerville area	3	3	– 3	4	4	– 4
New York	Tompkins County	2	– 9	– 5	– 9	– 8	– 5
Wisconsin	Portage County	5	– 2	2	– 2½	– 3½	– 2
New York	Binghamton area	11	– 1	4	1	0	– 5
Mississippi	Montgomery County	8	4	– 1	– 1	– 4	– 4
Pennsylvania	Montgomery County	5	5	5	6½	4	– 5
Indiana	Tippecanoe County	2	– 9	10	9½	9	3
Missouri	Scotland County	11	0	7	0	3	– 4
Virginia	Hanover County	4	8	0	1	2	7
Texas	San Marcos area	14	4	8	0	8	8
Arkansas	Prairie County	26	26	5	– 1½	2	– 1
Mississippi	Pontotoc County	16	6	10	– 3	2	6
South Carolina	York County	15	8	8	– 6	– 6	10
Louisiana	Caddo Parish	15	21	3	0	1	– 11
Texas	Rusk County	13	7	6	– 1	2	1
Tennessee	Henderson County	5	21	1	– 8	– 12	– 8
Kentucky	McCracken County	18	6	– 3	– 4½	– 4	0
South Carolina	Cherokee County	18	11	– 4	– 4	– 5	– 5
Alabama	Lee County	23	28	– 3	– 5	– 4	2
Florida	Escambia County	52	35	8	– 1½	4	– 1
Georgia	Waycross area	32	21	2	– 1	0	0
Virginia	Louisa County	38	30	30	1	4	2
North Carolina	New Hanover County	40	19	14	7	9	5

State.	Locality.	Increase with potash.				Increase with nitrogen.			
		K. alone.	$\frac{(KP-P)+(KN-N)}{2}$	$\frac{KP+KN-PN}{2}$	KPN – PN.	N. alone.	$\frac{(NP-P)+(NK-K)}{2}$	$\frac{NP+NK-PK}{2}$	NKP – KP.
		P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Indiana	Newton County	11	7½	10	– 1	4	1½	5	– 6
Missouri	Crawford County	6	1	1	– 7	4	2½	6	– 2
Ohio	Westerville area	5	5½	– 1	– 9	4	10½	10	2
New York	Tompkins County	4	2½	6	9	21	17½	18	22
Wisconsin	Portage County	3	3	6½	8	12	9½	10½	12
New York	Binghamton area	7	5	5	0	6	8	12	7
Mississippi	Montgomery County	3	5½	5	5	8	12½	13	14
Pennsylvania	do	10	14	14	5	4	6½	5	– 5
Indiana	Tippecanoe County	8	4	0	– 6	14	17½	21	15
Missouri	Scotland County	24	16½	18	11	14	9	13	6
Virginia	Hanover County	8	9	10	19	16	16	16	25
Texas	San Marcos area	12	1½	6	6	23	11	14	14
Arkansas	Prairie County	10	3	6	3	12	5½	9	6
Mississippi	Pontotoc County	9	– 1½	6	10	28	14½	20	23
South Carolina	York County	0	0	13	30	24	21	12	28
Louisiana	Caddo Parish	13	9	9	– 2	24	22½	25	14
Texas	Rusk County	11	6	11	10	32	24	26	25
Tennessee	Henderson County	1	6	16	20	36	29	28	31
Kentucky	McCracken County	3	7	13	7	39	33½	30	34
South Carolina	Cherokee County	7	8	8	8	40	41	41	41
Alabama	Lee County	6	5½	6	14	35	32½	32	39
Florida	Escambia County	19	7½	12	6	20	10	15	10
Georgia	Waycross area	15	14	16	17	45	42	42	43
Virginia	Louisa County	26	9	24	22	44	26	40	38
North Carolina	New Hanover County	21	17½	22	19	65	58½	60	57

RELATION OF FERTILIZER REQUIREMENTS TO CHARACTER OF SOILS.

That soils vary greatly in their crop-producing capacity and in the degree to which they respond to fertilizers under field conditions has long been known as a result of experience and also as a result of carefully recorded field tests. This marked difference in the degree to which various soils respond to fertilizer treatments is the most striking feature manifested in the results recorded in the preceding tables. It has also been long contended that there is a relation between the origin and the character of the soil and the character of the fertilizer that would be required to produce good results. It is doubtful, however, if such a claim can be substantiated by observed facts over a large territory. It certainly is not borne out by the results obtained on the 220 soils here reported, except in case of the muck soils which uniformly respond to potash. In fact, the character of the fertilizer

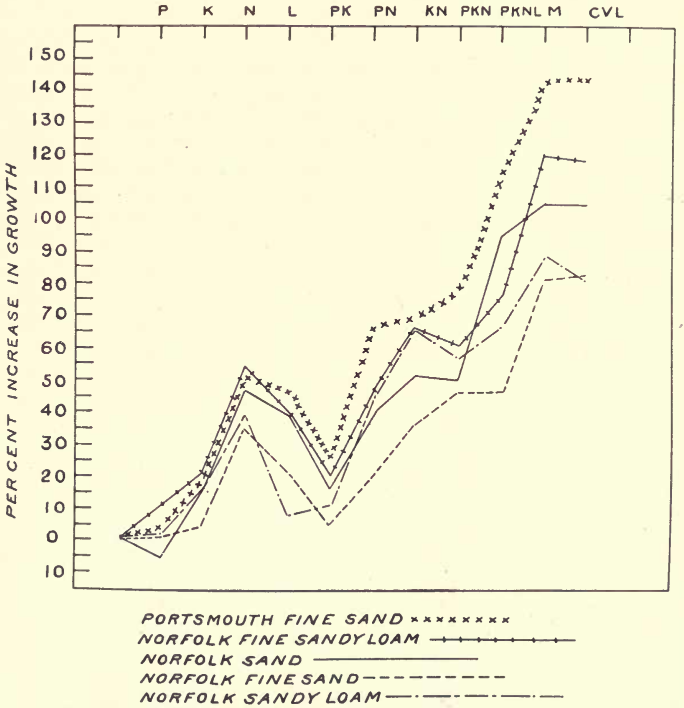


FIG. 1.—Percentage increase in growth of plants attributable to various fertilizer treatments of five principal soil types of the Waycross area, Georgia.

required for the same types or series of soils, as found in widely separated areas or localities, and as shown by these results, varies more than that required for different types and series when they occur in the same area or locality. In illustration of this point, five soils from Waycross, Ga., tested in triplicate, show a marked uniformity in the character of their manurial requirements, regardless of the fact that they represent five types and two soil series. The same soils in Escambia County, Fla., show manurial requirements of a very different character. (See Table III, p. 15, and figs. 1 and 2.)

In the Waycross area nitrate of soda is much more effective than sulphate of potash, and while lime is decidedly beneficial it is not equal to nitrate of soda. In Escambia County sulphate of potash is nearly as efficient as nitrate of soda, and lime is about twice as effective as the three fertilizer ingredients combined. These differences are based on average results for the two areas, and notwithstanding that the soils are of the same type, series, and formation, they show as marked differences in the character of fertilizer required as will be found between any of the areas, even when the soil types are entirely different.

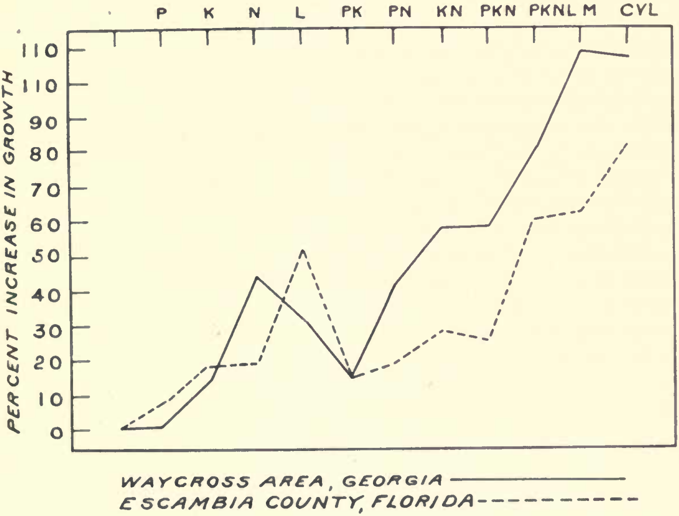


FIG. 2.—Percentage increase in growth of plants, attributable to various fertilizer treatments for soil of the Waycross area, Georgia, and Escambia County, Fla.

A Cecil sandy loam from Raleigh, N. C., was markedly improved by each of the three fertilizer salts, and also by lime, the increased growth of plants obtained when all of these ingredients were combined being 103 per cent. The same soil type from Lee County, Ala., as a result of tests on two samples, gave no response to either potash or phosphate, but produced a fair increase in growth as a result of nitrate of soda and also for lime, the maximum increase being 40 per cent where all three fertilizer salts were used in conjunction with lime. (See Table III, p. 15.)

RELATIVE EFFICIENCY OF FERTILIZERS BY LOCALITY.

In comparing the relative efficiency of the fertilizer ingredients, it is found that in the vast majority of instances nitrate of soda ranks first and lime second. This is especially true in the southern areas, where fertilizers are most extensively used. In the Central and Northern States, where the efficiency is less marked, there are quite a number of instances in which potash or phosphate outranks the lime or nitrate, although on an average the nitrate holds first rank and lime second. Sulphate of potash ranks next to lime, while acid phosphate having the lowest value, has in numerous instances shown a slightly negative effect.

With soils from the States of Wisconsin, Iowa, Missouri, Illinois, Indiana, Ohio, New York, and Pennsylvania the response to commercial fertilizers has been moderate, slight, or in many instances almost imperceptible. On those soils, also, organic manures, in the form of cowpea vines or stable manure, have been very much more effective than the chemical ones, the mean relative increase attributable to manure being nearly three times that for a complete fertilizer with lime, i. e., barnyard manure gave an average increase of 38 per cent, while the complete fertilizer with lime gave an average increase of only 13 per cent. (See Table XI, from which the averages were computed.) In these States lime alone seldom showed a marked effect. While the tests for these States are insufficient in number to represent all soil types and conditions, yet the results are in conformity with the general practices of the vast majority of farmers of these sections, who as a rule do not purchase commercial fertilizers for use in the growing of general farm crops, but who for the most part recognize the high value of barnyard manure and generally utilize all that is produced on the farm.

In the Atlantic and Gulf Coast States, including Kentucky, Tennessee, and Arkansas, for which a larger number of observations have been made and where most of the important soil types have been tested, the soils, with few exceptions, respond in a marked degree to commercial fertilizers and lime, and while cowpea vines and stable manure are on an average somewhat superior to commercial fertilizers, the differences between the relative value of these materials is small, being 54.7 and 58.6 per cent increase in growth for commercial fertilizers and manure, respectively, as compared with 13 and 38 per cent for the same materials in the former group of States. (See Table XI, rom which these averages were computed.) In other words, the ommercial fertilizers and lime are more than four times as effective n soils of the Altantic and Gulf Coast States as they are on those of the North Central States, including New York and Pennsylvania, while manure, when compared on the same soils, is only a half better on the soils from the former States. In this respect the results are again in conformity with the practices in the Atlantic and Gulf Coast States, where the bulk of the commercial fertilizers are used.

COMPARATIVE FERTILITY OF SOILS.

Another point brought out in the tables is the relative fertility or crop-yielding capacity of the untreated soils. Under the prevailing condition of crops and climate in the field, marked differences in this respect exist, some of the better soils showing a crop-producing capacity four or five times as great as that of the poorer ones. In these tests, where all soils are put into excellent physical condition and where moisture and temperature are always favorable, these differences are less marked but nevertheless exist to a considerable degree, as may be seen by comparing the actual weight of plants grown on the untreated soils. The average growth of plants on untreated soils from the North-Central States, including New York and Pennsylvania, is 28 per cent greater than the average of those from the Atlantic and Gulf Coast States. This difference in the initial crop-producing capacity of the soils from the two sections as indicated in the pots is sufficient to make the actual increase in growth from the stable manure nearly as great from one section as from the other.

TABLE XI.—*Increase in growth attributable to complete fertilizer with lime and manure; and proportionate cost of fertilizer to value of crops as obtained from Census, 1900.*

State.	Locality.	Weight of plants, untreated soil.	Increase from fertilizer and lime.	Increase from manure.	Cost of fertilizer to value of crop.
		Grams.	*Per cent.*	*Per cent.*	*Per cent.*
Missouri	Crawford County	9.6	0	19	0.23
Indiana	Newton County	8.8	4	56	.03
Ohio	Westerville area	7.8	8	28	.62
New York	Binghamton area	9.3	10	27	1.13
Wisconsin	Portage County	9.0	13	41	.32
Indiana	Tippecanoe County	6.8	16	37	.39
Mississippi	Montgomery County	9.3	18	18	.49
Pennsylvania	....do	10.1	19	17	3.28
New York	Tompkins County	7.9	10	46	1.98
Missouri	Scotland County	9.6	28	69	.08
Texas	San Marcos area	8.5	32	26	.04
Mississippi	Pontotoc County	6.8	38	24	.03
Arkansas	Prairie County	8.3	40	21	.72
Virginia	Hanover County	7.5	41	38	4.04
South Carolina	York County	6.2	43	72	6.34
Louisiana	Caddo Parish	6.3	45	54	.21
Texas	Rusk County	8.0	45	67	.29
Kentucky	McCracken County	5.0	48	70	.22
South Carolina	Cherokee County	7.2	55	64	5.54
Tennessee	Henderson County	7.5	57	72	.10
Florida	Escambia County	6.3	61	63	6.82
Alabama	Lee County	6.4	70	65	4.81
Georgia	Waycross area	6.0	90	108	4.45
Virginia	Louisa County	5.9	96	44	4.50
North Carolina	New Hanover County	5.2	107	131	7.82

RELATIVE RESPONSE TO FERTILIZERS AND EXPENDITURES FOR FERTILIZERS.

In Table XI, where the average percentage increase in growth attributable to the complete fertilizer and lime is given for each area and arranged in an ascending series, there is also given the average percentage increase attributable to stable manure for the same soils as well as the expenditure for commercial fertilizers for the same areas or counties. The expenditure for fertilizers in the area is expressed in percentage of the valuation of products other than those fed to live stock and is computed from statistics reported in the United States Census for the year 1900.

This table, besides showing the relative response to the chemical fertilizer and stable manure, which was discussed in preceding pages, also brings out the relation between the response to a complete fertilizer and lime, as obtained by the paraffin pot test, and the expenditure for fertilizer in each county or area expressed in percentage of the valuation of crops produced.

The table is separated into two portions, the first portion embracing 13 areas or counties in which the increase in growth attributed to a complete fertilizer and lime ranges from 0 to 40 per cent, and the second portion embracing 12 areas or counties in which the increased growth for the same treatment ranges from 41 to 107 per cent. In the first portion of the table there are no localities where the valuation of commercial fertilizer used equals 4 per cent of the value of the products grown, while in the second portion there are only four localities where it does not exceed such percentage. In the first portion of the table where the response to the fertilizer with lime does not exceed 40 per cent there are only three localities where the cost of fertilizer actually used in 1900 exceeded 1 per cent of the valuation of the crop grown. These exceptions are in New York and Pennsylvania, in areas where special crops probably receive more attention than in the others. The one in Pennsylvania was immediately about Philadelphia. Their nearness to both the great produce and fertilizer markets is also a factor tending to the more extensive use of fertilizers.

Of the four counties in the second portion of the table in which the cost of fertilizers used does not exceed 4 per cent of the value of crops grown, McCracken County, Ky., and Henderson County, Tenn., are each represented by only one sample. If better represented, they would probably fall in the first portion of the table, as indicated by the small amount of fertilizer used. The remaining two counties are Caddo Parish, La., and Rusk County, Tex., in each of which cases but little commercial fertilizer is used, though they are grouped in the second portion of the table as a result of their response to fertilizers in the pot test. In these two counties the soils were well represented by the samples tested, and the results indicate that the moderate use of commercial fertilizer might prove profitable. There are other factors, however, besides the comparative response to fertilizers which are concerned in their profitable use. Low value of land, long distance from markets and seat of supplies, including fertilizer, would all tend

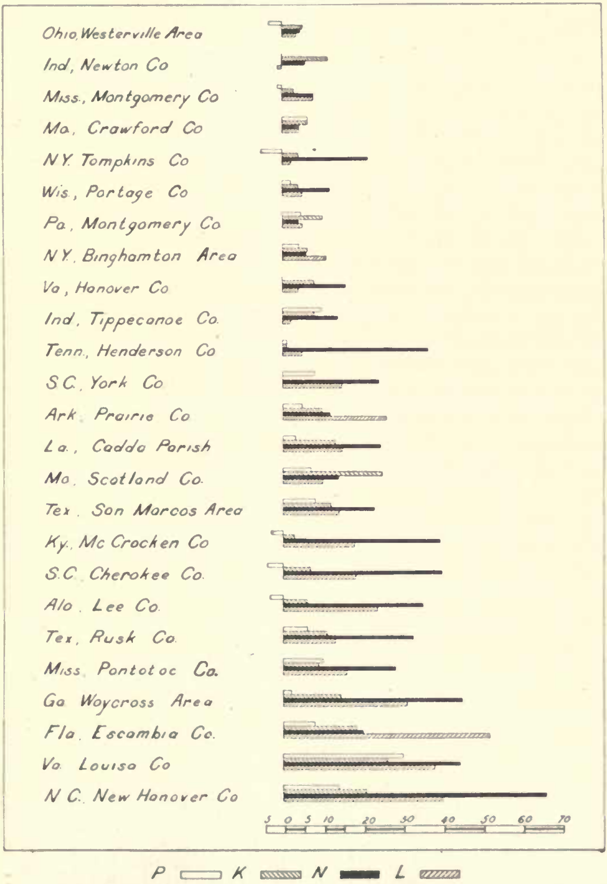


FIG. 3.—Percentage gain in plant growth attributable to each of the salts P, K, N, and L when used alone.

toward the unprofitable use of fertilizers. In Rusk County, Tex., and Caddo Parish, La., a few farmers have begun the use of commercial fertilizers and find them profitable.

AVERAGE EFFICIENCY OF FERTILIZER SALTS, BY LOCALITY.

Figure 3 shows graphically the percentage increase in growth attributable to each of the fertilizer salts and lime when used separately, and is based on the average for all soils of each area as given in Table X on page 43. The areas are arranged in an ascending series according to the aggregate increase from all ingredients, which ranges from a minimum of only 9 per cent for the Westerville area, Ohio, to a maximum of 140 per cent for New Hanover County, N. C. The range in the efficiency of the individual salts is also marked, the increase attributable to nitrate of soda varying from 4 per cent in several of the areas in the upper part of the diagram to 65 per cent in New Hanover County, N. C., and that for lime varying from a slightly negative result for Newton County, Ind., to an increase of 52 per cent for Escambia County, Fla., with somewhat lesser variations for potash and phosphorus. In the majority of the areas the efficiency of the three fertilizer ingredients and lime assume the same order. In 16 of the 25 areas, nitrate of soda was the dominant salt, while lime was dominant in 3 and potash in 3 of the areas. In 14 areas out of 25 lime ranks second in efficiency. In the States of Indiana, Missouri, Pennsylvania, and Virginia potash seems to have been relatively more effective than elsewhere. In the Arkansas and Florida areas lime is largely responsible for their position in the series, and in both of them nitrate of soda holds a relatively low rank.

TABLE XII.—*Average percentage increase in growth for all fertilizers and combinations, by soil series.*

Soil series.	No. of soils.	Weight of plants grown on untreated soil.	Increase in growth attributable to—										
			P.	K.	N.	PK.	PN.	KN.	PKN.		PKNL.	M.	CvL.
		Grams.	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*	*P.ct.*
Portsmouth	7	5.2	10	19	43	25	53	63	68	43	96	100	117
Norfolk	45	6.3	6	16	35	16	34	47	45	28	64	76	83
Cecil	12	6.0	14	12	36	17	32	46	52	26	69	62	65
Orangeburg	18	8.0	2	4	20	8	23	23	31	11	37	42	44
Miami	8	7.9	5	9	11	4	15	18	19	4	19	44	17
Marshall	5	7.0	5	8	16	6	10	20	12	4	8	50	8
Muck	4	6.0	21	62	27	56	33	49	60	30	60	46	39

TABLE XIII.—*Percentage increase in growth attributable to each fertilizer salt and to lime when used alone, as compared with its calculated effect when used in various combinations. Averages for each of six series and Muck.*

Soil series.	L.		P.				K.				N.			
	L, alone.	PKNL−PKN.	P, alone.	$\frac{(PK-K)+(PN-N)}{2}$	$\frac{PK+PN-KN}{2}$	PKN−KN.	K, alone.	$\frac{(KP-P)+(KN-N)}{2}$	$\frac{KP+KN-PN}{2}$	KPN−PN.	N, alone.	$\frac{(NK-K)+(NP-P)}{2}$	$\frac{NK+NP-KP}{2}$	NPK−PK.
Portsmouth..	43	28	10	8	7½	5	19	17½	17½	15	43	43½	45½	43
Norfolk.....	28	19	6	−½	1½	−2	16	11	14½	11	35	29½	32½	29
Cecil........	26	17	14	½	1½	6	12	6½	15½	20	36	26	30½	35
Orangeburg..	11	6	2	3½	4	8	4	4½	4	8	20	20	19	23
Miami........	4	0	5	−½	½	1	9	3	3½	4	11	9½	14½	15
Marshall.....	4	−4	5	−4	−2	−8	8	2½	8	2	16	8½	12	6
Muck........	30	0	21	0	20	11	62	28½	36	27	27	−½	13	4

COMPARATIVE EFFICIENCY OF FERTILIZERS, BY SOIL SERIES.

Table XII gives the average percentage increase in growth attributable to each fertilizer salt and combination of salts, by soil series, using only those in which the treatments were uniform and complete. No series were used where less than 5 samples were available, except in the case of Muck, in which only 4 samples were used.

Table XIII gives the percentage increase in growth attributable to each of the three fertilizer ingredients and lime, as compared with their effect when used in the combinations, the efficiency in the combinations being calculated by the difference method previously explained. These two tables show that the relative efficiency of the three salts and lime is essentially the same for all the soil series except the Muck. The range of efficiency of the complete fertilizer with lime is very marked, varying from a maximum of 96 per cent for the Portsmouth series to only 8 per cent for the Marshall series. It is noticeable that barnyard manure is relatively much more efficient for the Marshall and Miami series than for the others.

Figure 4 shows graphically the average relative percentage effectiveness of the three fertilizer ingredients and lime by series when used separately, as given in Table XIII. The variation in the aggregate effectiveness of the three salts and lime for the several series is nearly as great as when the soils were grouped by localities. It is evident, however, that the serial grouping is, to some extent, a locality grouping also, the Marshall and Miami series, which are the least responsive to the commercial fertilizers, occurring only in those States in which fertilizers are but little used, while the Portsmouth and Norfolk series are confined wholly to the Atlantic seaboard, where fertilizers are most extensively used. While there is a marked difference in the aggregate effectiveness of the three salts and lime on different series, ranging from a minimum of 29 per cent for the Miami series to a maximum of 115 per cent for the Portsmouth series, broadly speaking the relation between the value of the individual ingredients in the several series is remarkably uniform, even more so than occurs when the soils are considered by areas. The Muck, represented by only 4 samples, is exceptional, and shows the characteristic importance of potash, that ingredient being on the average about as effective as the total of lime, nitrogen, and phosphate. This fact is also in conformity with our field knowledge of Muck and Peat, which are greatly benefited by applications of potash salts.

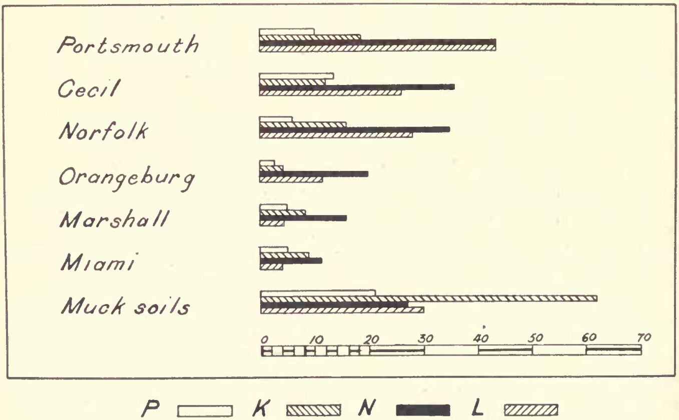


FIG. 4.—Relative efficiency of fertilizer ingredients by soil series, when the ingredients are used alone.

TABLE XIV.—*Average percentage increase in growth attributable to each fertilizer salt and lime for soils of the Norfolk, Portsmouth, Orangeburg, and Cecil series when classified by texture.*

Soil class.	Number of soils.	L.		P.				K.				N.			
		L, alone.	PKNL−PKN.	P, alone.	$\frac{(PK-K)+(PN-N)}{2}$	$\frac{PK+PN-KN}{2}$	PKN−KN	K, alone.	$\frac{(KP-P)+(KN-N)}{2}$	$\frac{KP+KN-PN}{2}$	KPN−NP.	N, alone.	$\frac{(NP-P)+(NK-K)}{2}$	$\frac{NP+NK-KP}{2}$	NKP−KP.
Coarse sand	2	14	9	−10	− 10	−4	7	8	5	8	19	34	26	24	35
Sand	12	43	33	7	−1.5	2	−1	16	10	16	13	42	32.5	35	32
Fine sand	17	33	21	5	2.5	3	3	15	13.5	15	15	37	35	36	36
Sandy loam	17	14	11	6	0	0	4	9	7	11	15	27	24	27	31
Fine sandy loam	25	22	13	8	3	5	0	13	8.5	10	6	27	23.5	26	22

EFFICIENCY OF FERTILIZER AS RELATED TO SOIL TEXTURE.

Table XIV gives the response to each of the three salts and lime when used alone and when in the various combinations for soils of the Norfolk, Portsmouth, Cecil, and Orangeburg series when grouped by the variation in texture. This grouping of the soil fails to bring out any variations in the character of the fertilizer required for the different textures, but it does show in general that the finer the texture of the soil, the less marked is the effect of the various fertilizer salts or the aggregate effect of them all.

NATURAL FERTILITY AS RELATED TO RESPONSIVENESS TO FERTILIZERS.

Another comparison brought out in the general tables is the relation between the crop-producing capacity of the untreated soils in the pots and their response to fertilizers. In general, the lower the crop capacity, the greater the response to fertilizers or manure, and vice versa.

Table XV shows the average effectiveness of a complete fertilizer and lime on soils arranged in groups according to the weight of plants grown when untreated, and it is shown that there is a gradual and consistent decrease in the effect of the treatment, as the untreated soils are capable of producing larger plants.

TABLE XV.—*Showing decreasing effect of fertilizers with increasing productiveness in untreated samples.*

Number of soils.	Weight of plants on untreated soil.	Average gain attributable to fertilizers.
	Grams.	*Per cent.*
23	3 to 4.9	87.9
35	5 to 5.9	68.3
25	6 to 6.9	41.8
46	7 to 7.9	40.1
33	8 to 8.9	23.9
19	9 to 9.9	26.8
9	10 to 10.9	13.0
9	11 to 11.9	8.4
7	12 and over	3.9

It is significant that the sandy soils of the Norfolk and Portsmouth series, collected from the Southern States where wheat is seldom grown, have produced on an average larger and more thrifty wheat plants by the application of a complete fertilizer and lime, than have been produced by the same or other treatments on soils of the Marshall or Miami series from Wisconsin, Ohio, Indiana, and New York, where wheat does well. This fact is in harmony with the view now gaining prevalence, that the variation in the character and composition of the mineral matter of soils is of minor importance as regards crop adaptation and yielding capacity, except so far as character of material influences condition of the soil in its relation to soil moisture and permeability to air, water, and the roots of plants. In other words, crop adaptation and crop-producing power depend more upon climatic environment and physical condition of the soil than upon soil type or the geological formation from which it is derived. The best wheat soils or those best suited to peaches or to truck crops are not so solely by virtue of the character of the mineral matter of which they are composed, but because there are present climatic and soil conditions that enable those classes of plants to attain perfection.

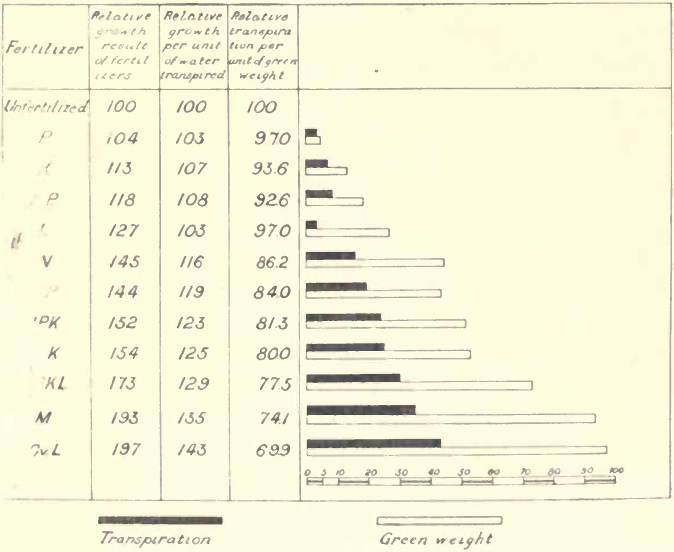
The poorest soils, by proper manipulation and the addition of suitable manure or fertilizer, can be made to produce as large yields in the pots as can be procured by the same or other treatments on the best soils that occur, and yet such applications have but slightly altered the composition of the soil. Such improvement does not involve any considerable length of time, but may be brought about in a few days or at most a few weeks. This does not mean that would be either feasible or practical to attempt such a radical chan under field conditions in so short a time. The expense invol would not justify the procedure, neither would the soil be able maintain such an ideal condition under the adverse climatic co tions which might prevail or against the poor systems of farming vogue. The improvement of soil conditions in the field becomes a purely business proposition in which the expense involved must n exceed probable returns.

Important in this connection is the assembling and association o all those factors that will work together for the good of the soil, such as the selection of suitable crops, the use of a proper rotation, the adoption of catch and winter cover crops, and cultivation of such character that erosion will be reduced to a minimum and the rainfall absorbed and retained in ample supply. By such procedure the condition of a soil will in time become greatly modified and its fertility improved. So-called soil robbery is, after all, more properly soil mutilation, brought about by the carelessness of man.

FERTILIZERS AND ECONOMY OF WATER IN PLANT GROWTH.

It has been stated that no attempt will be made to explain how fertilizers effect an increase in plant growth, yet there is one point which has been established as a result of this investigation of which mention should be made. It is the relation between growth, as effected by fertilizers, and water transpired by the plants or used in the process of their growth. In all of the tests a careful record has been kept of the water transpired for each of the 13,000 or more pots. As a result of such observations, it has been found that as fertilizers increase plant growth, there is a marked diminution in the water transpired per unit of growth; or, putting it in the reverse order, there is a marked increase in growth for a unit of water used, and such increase becomes greater as the fertilizers are more effective. As a result of computations for twenty soils taken at random, it was found that the percentage increase in growth for a unit of water used equaled, approximately, one-half of the total increase in growth resulting from the fertilizer treatments.

Figure 5 gives the average results for 20 soils and shows not only the gain in growth following the fertilizer treatments, but also shows the associated increase in growth per unit of water transpired.



Fertilizer	Relative growth result of fertilizers	Relative growth per unit of water transpired	Relative transpiration per unit of green weight
Unfertilized	100	100	100
P	104	103	97.0
[illegible]	113	107	93.6
P	118	108	92.6
[illegible]	127	103	97.0
V	145	116	86.2
P	144	119	84.0
PK	152	123	81.3
K	154	125	80.0
KL	173	129	77.5
M	193	135	74.1
[illegible] L	197	143	69.9

FIG. 5.—Percentage increase in growth of plants attributable to fertilizer and accompanying increase per unit of water transpired. Average of 20 soils.

Excepting lime, in the presence of which transpiration remains nearly normal, the different fertilizer constituents show no marked variation in respect to this phenomenon. Lime frequently produces an increase in growth and yet the plants maintain practically the same rate of transpiration per unit of growth as that observed for the untreated soil.

In a few miscellaneous tests, where the different forms of potash were tried, it was found that kainit and muriate of potash decreased the rate of transpiration per unit of growth, as compared with sulphate of potash.

While these observations have no economic significance in the pots where moisture content is always ample, they may be of considerable importance in relation to the use of fertilizers in the field and explain, in part, the benefits derived therefrom. It frequently happens, owing to scanty rainfall, or a low water-holding capacity of the soil, that the available water supply is the limiting factor in crop yields. Where such conditions exist, and they occur frequently in all parts of the country, the presence of a fertilizer which would enable the crop to economize in its water consumption would be of considerable importance and might, as pointed out above, enable the crop to make a marked increase in growth despite the limited water supply.

SUMMARY.

The paraffin-pot method of testing the manurial requirements of soils, used in these investigations, while not designed to supersede field tests, is admirably adapted to an investigation of this kind and is very useful as a method of indicating what fertilizers should be used in the field.

The results obtained in the pots with the various ingredients are relatively the same as those obtained in the field, but may differ in degree. This is true of all ingredients commonly used except the phosphates, which give a relatively lower effect in the pots than the others. The absolute effect is usually greater in the field than in the pots and phosphates may frequently be economically used where their benefits are not indicated by the pots.

The results obtained in the pots generally agree with the fertilizer practices in the various sections from which the soils were secured. In the North Central States, where but little commercial fertilizer is used, and where the main dependence is placed upon barnyard manure, the pot tests show manure to be three times as efficient as the fertilizer. In the Atlantic seaboard and Gulf Coast States, where but little manure is available, and where the main dependence is upon commercial fertilizers, the manure as tested in the pots has been only slightly superior to the fertilizers. Muck, quite generally recognized as in need of potash in the field, has shown that ingredient to be nearly as efficient as lime, nitrate, and phosphate combined, as determined by the pot tests.

Transpiration, while a good indicator of the relative growth of plants when under like conditions, usually gives a range of lesser magnitude than the variation by green weights.

The green weight of plants grown for about twenty-five days in the pots occasionally equals or exceeds 1 per cent of the weight of the soil in which they grew. Such plants contain about 85 per cent of water and transpire approximately 100 grams of water for each gram of green matter produced. The dry matter of such plants is richer in mineral constituents and nitrogen than that of the same plants if matured. The draft on the water and mineral constituents of the soil under these conditions is greater than that occasioned by the removal of a large and matured crop under field conditions.

As an average of all tests, the organic manures have outranked the chemical ones. Barnyard manure and cowpea vines with lime tie for first rank. The three chemical salts with lime rank third and the same salts without lime rank fourth.

Of the combinations of chemical salts the order of efficiency is as follows: The three salts with lime, first; three salts alone, second; potash and nitrate, third; phosphate and nitrate, fourth, and phosphate and potash, fifth.

Of the salts used individually the order is nitrate, lime, potash, and phosphate; nitrate being the most efficient and phosphate the least efficient.

As an average result of all tests, nitrate of soda has produced a marked increase in growth which has not been further increased by the addition of acid phosphate. Potash has produced a moderate increase in growth and when supplemented by nitrate the effect has been slightly less than the aggregate of these two ingredients when used separately. The efficiency of the combination of nitrate and potash has not been appreciably improved by the addition of phosphate.

Lime alone has generally produced a marked increase in growth and has usually increased the efficiency of a complete fertilizer. There is but little evidence that the benefits derived from lime are due to beneficial action on nitrification.

Soils vary greatly in crop-producing capacity as found under field conditions. Part of such variation is due to physical condition and consequent relation to water, and is largely overcome in the pots. After these conditions are largely equalized in the pots marked differences in crop-yielding capacity still exist to such an extent that good soils may produce four or five times as large a growth as that produced on very poor soils under the same conditions. By the application of suitable manures or fertilizers these differences are overcome, and in the pots the poorest soils when treated with suitable substances become as productive as the best ones.

Soils vary greatly in the degree to which they respond to commercial fertilizers, lime, manure, and green manure. In general, the degree of response varies inversely as the crop-yielding capacity and ranges from zero to several hundred per cent. The soils of the Atlantic and Gulf Coast States are much more responsive than those of the Central and Northern States.

In 60 per cent of the soils here tested, each fertilizer salt appears to have a special function, so far as it influences the growth of plants, which is not materially modified by the addition or withholding of the other salts. In 29 per cent of the soils the functions of the several salts, as affecting the growth of plants, are more or less interchangeable, there being quite a number of instances when each salt used alone gave as large an increase in growth as was secured by combining three of them. In 11 per cent of the soils each salt not only has a distinct function, but it is dependent upon the presence of others for its fullest effect as shown by a much greater efficiency when used in combination than when used alone. There is no apparent relation either by soil type or by locality to this grouping of the soils.

The variation in the efficiency of a fertilizer salt as used alone and in combination with various other salts bears no consistent relation to the efficiency of the associated salts or to the efficiency of the combination as a whole.

In the pots, as an average of all tests, the aggregate efficiency of the several salts when used separately is slightly greater than when the same salts are used in combination. Under field conditions, as an average of many tests, the aggregate of individuals is the same as when used in combination. Individual soils show wide variation in respect to this point.

The character of fertilizer indicated for a specific soil type as it occurs in widely separated localities usually varies more than that for very different types when in the same locality and subjected to similar environment.

The character of fertilizer indicated for various soil series is essentially the same, although the response to such a fertilizer varies greatly.

In general, the finer the texture of soils the less responsive are they to fertilizers, although the character of fertilizer indicated remains the same.

With few exceptions the character of fertilizer required for soils depends more upon local conditions and practices than it does upon the type of soil or the geological formation to which it belongs. The Muck soils are an exception and show a universal response to potash salts.

The condition of the soil is of greater importance than its chemical composition.

Without materially changing the composition of the soil, poor soils by proper manipulation and suitable applications can be made to produce as large crops in the pots as can be grown on the best soils by the same or other treatments.

Fertilizers when effective aid plants to economize in the use of water.

In conclusion it may be said that the crop-yielding capacity of soils is increased by improving their physical condition and by supplying manures or fertilizers. Frequently both are necessary, and the latter may assist the former. By the employment of both methods poor soils may become as productive as the best ones. There is but little to indicate any relation between the formation and character of the soil and character of fertilizer to which it will respond. Usually soils of a limited locality, where climatic condition and farm practices are uniform, show but little difference in the character of fertilizer required, although the degree of response may vary greatly for different fields, making their use profitable in some instances and unprofitable in others. Except in the most general way, the fertilizer requirement of soils becomes a problem for each farm or for each class of farms under like conditions of soil, climate, and system of cropping and fertilization. The indications are that fertilizers containing relatively more potash and nitrogen than do those now in general use would prove more effective. This conclusion (to which exception might be taken by some because of the fact that phosphates are known to be economically used on some soils that fail to respond to that salt in the pots) is not based alone on the result of this investigation, but upon the tendency of the more progressive planters to use a higher grade fertilizer, i. e., one containing relatively more nitrogen and potash than that used in the past. Lime has proved quite generally beneficial, being on an average more effective than both potash and phosphate.

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BUREAU OF SOILS—BULLETIN No. 49.
MILTON WHITNEY, Chief.

THE ACTION OF WATER AND AQUEOUS SOLUTIONS UPON SOIL CARBONATES.

BY

FRANK K. CAMERON AND JAMES M. BELL.

WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1907.

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LETTER OF TRANSMITTAL.

United States Department of Agriculture,
Bureau of Soils,
Washington, D. C., July 20, 1907.

Sir: I transmit herewith a technical paper by Frank K. Cameron and James M. Bell, entitled The Action of Water and Aqueous Solutions upon Soil Carbonates, which I recommend to be published as Bulletin No. 49 of this Bureau. The manuscript has been gone over with Assistant Secretary Hays, who authorizes me to state that he concurs in my recommendation for its publication.

Very respectfully,

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

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THE ACTION OF WATER AND AQUEOUS SOLUTIONS UPON SOIL CARBONATES.

INTRODUCTION.

Lime as a mineral constituent of soil amendments or fertilizers has always occupied a prominent place in soil chemistry. It is usually applied to the soil as a sulphate (gypsum or land plaster), phosphate, hydrate (or oxide), or carbonate. The solubility of these substances is obviously of the utmost importance in determining their distribution and effectiveness when applied to the soil. Nevertheless, the literature regarding their solubilities has been most confusing and contradictory, and in consequence agricultural investigations have suffered seriously in that observations have been interpreted in the light of uncertain or conflicting premises. In many cases, indubitably, the truth has been missed on this account and conclusions deduced which have not only delayed or misguided scientific investigation, but have led to serious disappointment when brought under the test of actual farm practice. For these reasons the investigation of the fundamental solubility data and the chemical relations between the lime salts and aqueous solutions has been deemed necessary in the studies which this Bureau is prosecuting on soils and fertilizers.

The present state of our knowledge as regards the solubility of the sulphate[a] and the phosphates[b] of calcium has been shown in recent publications of the Bureau. The present bulletin contains similar data for the hydrates and carbonates of lime; and since magnesia and its compounds are so closely related to lime and its corresponding compounds, both in chemical properties and mineral associations, data for the hydrates and carbonates of magnesia are also included. In searching the literature for the material contained in this bulletin an enormous number of papers was found, especially with regard to the solubility of lime carbonates. Many of these, however, it has not been deemed wise to cite—when they had only a local or fugitive interest, when they were of a qualitative nature only, when they would add but further and unnecessary confirmation to points brought out by other data cited, or when, as occasionally happened, they were obviously trivial or of doubtful accuracy. It is believed, however, that the data given will furnish an approximately complete statement of our present knowledge of the subject. It is also believed that this material will have an interest for geologists and certain technical manufacturers second only to that for agriculturists.

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[a] Bul. No. 33, Bureau of Soils, U. S. Dept. Agr. (1906).

[b] Bul. No. 41, Bureau of Soils, U. S. Dept. Agr. (1907).

One of the great agricultural problems of the United States is the alkali, or accumulation of soluble salts frequently found in the soils of the arid areas of some of the Western States, and to a proper understanding and satisfactory handling of this important practical problem, a knowledge of the chemistry of the solutions formed by the action of water on the mineral components of these soils is of fundamental importance. The chemistry of "white alkali" has been treated quite fully in previous publications of this Bureau and especially the important reactions between gypsum and solutions of the more soluble salts found in the soil. The present bulletin brings together our knowledge of the reactions between the same solutions and calcium carbonate, the immediate source of the much-dreaded "black alkali." An intelligent interpretation can now be made of the analyses of drainage waters and the changes in the soil which they indicate. A scientific foundation is now prepared for the further development of practical methods for handling this important agricultural problem.

CARBON DIOXIDE.

SOLUBILITY OF CARBON DIOXIDE IN WATER.

The solubility in water of carbon dioxide, like all other gases, is greater at the lower temperatures than at the higher temperatures. With one or possibly two known exceptions, the solubility in aqueous solutions is decreased by increasing quantities of the material in solution. Thus, the solubility of carbon dioxide in water is decreased either by increasing the temperature or by the addition of some material, such as sodium chloride or other salts. The results of the work recorded in the literature have been assembled and are given in the following tables. The results are given in the same form as they have been recorded in the original papers. For instance, the solubility of carbon dioxide in water at 10° C. has been given by Bunsen as 1.1847. This means that one cubic centimeter of water at 10° will dissolve the quantity of carbon dioxide occupying 1.1847 cubic centimeters at 0° and 760 mm. *All the gaseous volumes are reduced to 0° and 760 mm. pressure.* In this way comparisons may be made between the solubility of the gas in solvents at different temperatures and also in different solutions.

TABLE I.—*Solubility of carbon dioxide in water at different temperatures.*

Temperature.	Bunsen.[a]	Setschenow.[b]	v. Wroblewski.[c]	Bellati and Lussana.[d]	Bohr and Beck.[e]	Prytz and Holst.[f]	Bohr.[g]	Geffcken.[h]
° C.								
0	1.7967		1.797			1.7308	1.713	
1	1.7207						1.646	
2	1.6481						1.548	
3	1.5787						1.527	
4	1.5126						1.473	
5	1.4497						1.424	
6	1.3901						1.377	
7	1.3339						1.331	
8	1.2809						1.282	
9	1.2311						1.237	
10	1.1847						1.194	
10.75				1.1281				
11	1.1416						1.154	
12	1.1018						1.117	
12.43			1.086					
12.68				1.0414				
13	1.0653						1.083	
14	1.0321						1.050	
15	1.0020						1.019	1.070
15.2		1.0090						
16	.9753						.985	
17	.9519						.956	
17.1		.9619						
17.6		.932						
18	.9318						.928	
18.38		.896						
19	.9150						.902	
19.3		.885						
20	.9014						.878	
21		.838					.854	
21.7		.825						
22							.829	
22.17				.8375				
22.4	.8642							
23		.798					.804	
24							.781	
25							.759	.8255
26							.738	
27							.718	
28							.699	
29							.682	
30							.665	
35							.592	
37.29					0.5629			
40							.530	
45							.479	
50							.436	
55							.394	
60							.359	
100					.2438			

[a] Ann. Chem. Pharm., **93**, 1 (1855); Phil. Mag. (4), **9**, 116, 181 (1855).

[b] Arch. gesammt. Physiol., **8**, 1 (1874); Mémoires de l'acad. impér. des s. i. de St.-Pétersb. (7), **22**, No. 6 (1875); **34**, No. 3 (1886); **35**, No. 7 (1887); Ann. Chim. Phys. (6), **25**, 226 (1892).

[c] Ann. Phys. Chem., **254**, 290 (1883).

[d] Atti Ist. Veneto (6), **7** (1889); abstr. in Beibl. Ann. Phys. Chem., **14**, 18 (1890).

[e] Ann. Phys. Chem., **280**, 318 (1891).

[f] Ann. Phys. Chem., **290**, 130 (1895).

[g] Ann. Phys. Chem., **304**, 500 (1899).

[h] Zeit. phys. Chem., **49**, 257 (1904).

TABLE II.—*Solubility of carbon dioxide in water under different pressures.*[a]

Pressure.	Solubility at—	
	0° C.	12.43° C.
Atmospheres.		
1	1.797	1.086
5	8.65	5.15
10	16.03	9.65
15	21.95	13.63
20	26.65	17.11
25	30.55	20.31
30	33.74	23.25

[a] v. Wroblewski, Ann. Phys. Chem., **254**, 290 (1883).

It will be seen that at the higher pressures the solubility of carbon dioxide in water is not proportional to the pressure as would be expected from Henry's law. At the lower pressures, below 5 atmospheres, the solubility is almost proportional to the pressure.

SOLUBILITY OF CARBON DIOXIDE IN AQUEOUS SOLUTIONS.

Sulphuric acid.

TABLE III.—*Solubility of carbon dioxide in aqueous solutions of sulphuric acid.*[a]

H_2SO_4 per liter.	Solubility at—	
	15° C.	25° C.
Grams.		
25.1	1.016	0.7923
25.3	1.016	.7936
47.8	.9772	.7693
50.9	.9775	.7685
52.3	.9756	.7672
95.8	.9175	.7302
102.3	.9143	.7273
185.7	.8354	.6736
186.2	.8385	.6747

[a] Geffeken. Zeit. phys. Chem., **49**, 257 (1904).

TABLE IV.—*Solubility of carbon dioxide in various mixtures of sulphuric acid and water at 17° C.*[a]

H_2SO_4 in solution.	Solubility.	H_2SO_4 in solution.	Solubility.
Per cent.		*Per cent.*	
100.0	0.932	81.5	0.660
96.8	.852	73.1	.705
92.0	.719	8.58	.857

[a] Setschenow, Mélanges phys. et chim. du bul. de l'acad. impér. des sci. de St.-Pétersb., **9**, 617 (1876), Ann Chim. Phys. (6), **25**, 226 (1892).

Tables III and IV show that in the comparatively weak solutions of sulphuric acid the solubility of carbon dioxide is decreased by increasing that concentration. On the other hand, starting from sulphuric acid (100 per cent H_2SO_4) the solubility of carbon dioxide is decreased by the addition of water, in which the solubility of the gas is less than in either sulphuric acid or pure water.

Nitric acid.

TABLE V.—*Solubility of carbon dioxide in aqueous solutions of nitric acid.*[a]

HNO_3 per liter.	Solubility at—	
	15° C.	25° C.
Grams.		
29.7	1.073	0.8382
29.9	1.075	.8366
35.1	1.069	.8387
44.4	1.080	.8447
87.1	1.093	.8620
87.4	1.093	.8622
117.2	1.105	.8752
158.7	1.109	.8839
160.0	1.111	.8865

[a] Geffcken, Zeit. phys. Chem., **49**, 257 (1904).

Nitric acid solutions form the striking exception to the generality hat the solubility of carbon dioxide is decreased by the addition of some other solute. It will be seen from Table V that the solubility of carbon dioxide is increased by adding nitric acid to the solution.

Hydrochloric acid.

TABLE VI.—*Solubility of carbon dioxide in aqueous solutions of hydrochloric acid.* [a]

HCl per liter.	Solubility at—	
	15° C.	25° C.
Grams.		
18.2	1.041	0.8047
18.7	1.042	.8074
44.2	1.020	.7973
45.6	1.023	.7984
75.9	0.9864	.7951
79.6	1.009	.7951

[a] Geffeken, Zeit. phys. Chem., **49**, 257 (1904).

Citric acid.

TABLE VII.—*Solubility of carbon dioxide in aqueous solutions of citric acid at 15.2°.* [a]

Citric acid per liter.	Solubility.	Citric acid per liter.	Solubility.
Grams.		*Grams.*	
12	1.007	198	0.893
49	.975	298	.841
99	.950	595	.719

[a] Setschenow, Ann. Chim. Phys. (6), **25**, 226 (1892).

Sodium chloride.

TABLE VIII.—*Solubility of carbon dioxide in aqueous solutions of sodium chloride at different temperatures.*

Temperature.	6.52 [a] per cent solution.	7.062 [b] per cent solution.	12.995 [b] per cent solution.	17.42 [b] per cent solution.	17.62 [a] per cent solution.	26.00 [b] per cent solution.	5 [c] per cent solution.
° *C.*							
0	1.234	....	....	....	0.678	....	....
5	1.024	....	....	....	.577	....	....
6.4	....	0.8900	0.6326	0.5181	....	0.3470	....
10	.875	....	....	....	.503	....	....
15	.755	.7347	.5569	.4306	.442	.2969	0.8122
20	.664	....	....	....	.393	....	....
22	....	....	.4822	.3892	....	.2630	....
25	.583	....	....	....	.352	....	....
30	.517	....	....	....	.319	....	....
35	.460	....	....	....	.288	....	....
40	.414	....	....	....	.263	....	....
45	.370	....	....	....	.235	....	....
50	.335	....	....	....	.215	....	....
55	.305	....	....	....	.198	....	....
60	....	....	....	....	.183	....	....

[a] Bohr, Ann. Phys. Chem., **304**, 500 (1899).
[b] Mackenzie, Ann. Phys. Chem., **237**, 438 (1877).
[c] Setschenow, Arch. gesammt. Physiol., **8**, 1 (1874).

TABLE IX.—*Solubility of carbon dioxide in aqueous solutions of sodium chloride.*[a]

NaCl per liter.	Solubility at—		
	15.2° C.	18.38° C.	21.7° C.
Grams.			
32	0.866	0.795	0.726
64	.760	.702	.630
96	.661	.610	.560
128	.580	.533	.497
160	.515	.483	.437
192	.466	.427	.394

[a] Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22,** No. 6 (1875); Ann. Chim. Phys. (6), **25,** 226 (1892).

TABLE X.—*Solubility of carbon dioxide in aqueous solutions of sodium chloride at 15.2° C.*[a]

NaCl per liter.	Solubility.	NaCl per liter.	Solubility.
Grams.		*Grams.*	
12.9	0.978	78.9	0.728
18.6	.950	105.2	.640
19.7	.944	125.6	.606
25.9	.919	157.8	.530
38.8	.865	210.4	.422
52.6	.802	315.6	.290
63.1	.778		

[a] Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **34,** No. 3 (1886); Ann. Chim. Phys. (6), **25,** 226 (1892).

In Table XI there have been collected several isolated determinations by Setschenow, which are given for the sake of completeness.

TABLE XI.—*Solubility of carbon dioxide in aqueous solutions of sodium chloride.*[a]

Composition of solution.	Solubility at—		
	15.2° C.	18.38° C.	21.7° C.
125.6 grams NaCl per liter (A)	0.606	0.550	....
100 c. c. solution A + 95.6 grams water	.776	.705	....
100 c. c. solution A + 296.8 grams water	.885	.807	....
11.7 per cent solution	....	....	0.489
19.7 per cent solution	....	....	.341

[a] Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); **34**, No. 3 (1886).

Potassium chloride.

TABLE XII.—*Solubility of carbon dioxide in aqueous solutions of potassium chloride at different temperatures.*[a]

Density of solution.	KCl in solution.	Solubility at—		
		8° C.	15° C.	22° C.
	Per cent.			
1.0211	6.06	0.9880	0.7772	0.6701
1.0527	8.65	.9178	.7768	.6488
1.0796	11.97	.8639	.7202	.5970
1.1488	22.51	.6877	.5707	.4801

[a] Mackenzie, Ann. Phys. Chem., **237,** 438 (1877).

TABLE XIII.—*Solubility of carbon dioxide in aqueous solutions of potassium chloride.*

Setschenow.[a]		Geffcken.[b]		
KCl per liter.	Solubility at 15.2° C.	KCl per liter.	Solubility at—	
			15° C.	25° C.
Grams.		*Grams.*		
94	0.819	31.55	0.9892	0.7695
141	.745	32.23	.9865	.7667
282	.579	77.96	.8875	.6920
.....	.....	78.93	.8910	.6961

[a] Ann. Chim. Phys. (6), **25.**, 226 (1892).
[b] Zeit. phys. Chem., **49**, 257 (1904).

One other determination has been made by Setschenow,[a] viz, that at 22.4° C. the solubility of carbon dioxide in 14.9 per cent potassium chloride solution is 0.589.

Ammonium chloride.

TABLE XIV.—*Solubility of carbon dioxide in aqueous solutions of ammonium chloride at different temperatures.*[a]

Density of solution.	NH_4Cl in solution.	Solubility at—		
		10° C.	15° C.	22° C.
	Per cent.			
1.0211	6.47	1.0227	0.8253	0.7182
1.0470	8.72	1.0000	.7906	.7022
1.0527	12.73	.9220	.7981	.6840
1.0721	22.23	.8132	.7384	.5998

[a] Mackenzie, Ann. Phys. Chem., **237**, 438 (1877).

TABLE XV.—*Solubility of carbon dioxide in aqueous solutions of ammonium chloride at 15.2° C.*[a]

NH_4Cl per liter.	Solubility.	NH_4Cl per liter.	Solubility.
Grams.		*Grams.*	
1.0	1.005	86	0.897
10.0	.985	129	.858
43.0	.956	172	.819
51.6	.941	258	.770
64.5	.931	.....	.....

[a] Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); **35**, No. 7 (1887); Ann. Chim. Phys. (6), **25**, 226 (1892).

In the first of the above papers Setschenow has recorded that at 21.7° C. the solubility of carbon dioxide in 17.8 per cent of ammonium chloride solution is 0.669.

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[a] Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875).

Cæsium and rubidium chlorides.

TABLE XVI.—*Solubility of carbon dioxide in aqueous solutions of the chlorides of cæsium and rubidium.*[a]

Solution.	Solubility at—	
	15° C.	25° C.
93.1 grams $CsCl$ per liter	1.000	0.777
58.1 grams $RbCl$ per liter	.991	.770
122.2 grams $RbCl$ per liter	.921	.717

[a] Geffeken, Zeit. phys. Chem., **49**, 257 (1904).

Lithium chloride.

TABLE XVII.—*Solubility of carbon dioxide in aqueous solutions of lithium chloride at 15.2° C.*[a]

$LiCl$ per liter.	Solubility.	$LiCl$ per liter.	Solubility.
Grams.		*Grams.*	
16.72	1.035	125.4	0.596
25.08	.899	250.8	.497
50.15	.808	501.5	.120

[a] Setschenow, Ann. Chim. Phys. (6), **25**, 226 (1892).

Sodium bromide.

TABLE XVIII.—*Solubility of carbon dioxide in aqueous solutions of sodium bromide at 15.2° C.*[a]

$NaBr$ per liter.	Solubility.
115.1	0.775
460.3	.364
690.4	.221

[a] Setschenow, Ann. Chim. Phys. (6), **25**, 226 (1892).

Potassium bromide.

TABLE XIX.—*Solubility of carbon dioxide in aqueous solutions of potassium bromide.*

Setschenow.[a]		Geffcken.[b]		
KBr per liter.	Solubility at 15.2° C.	KBr per liter.	Solubility at—	
			15° C.	25° C.
Grams.		*Grams.*		
83.9	0.908	65.51	0.9783	0.7621
167.7	.819	67.30	.9766	.7619
251.5	.748	125.8	.9100	.7030
503.1	.579	126.7	.9065	.7068

[a] Ann. Chim. Phys. (6), **25**, 226 (1892).
[b] Zeit. phys. Chem., **49**, 257 (1904).

Potassium iodide.

TABLE XX.—*Solubility of carbon dioxide in aqueous solutions of potassium iodide.*

Setschenow.[a]		Geffeken.[b]		
KI per liter.	Solubility at 15.2° C.	KI per liter.	Solubility at—	
			15° C.	25° C.
Grams.		*Grams.*		
319.1	0.773	93.85	0.9809	0.7678
478.6	.688	95.18	.9835	.7676
957.3	.506	173.24	.9144	.7236
		185.87	.9090	.7166

[a] Ann. Chim. Phys. (6), **25**, 226 (1892).
[b] Zeit. phys. Chem., **49**, 257 (1904).

Sodium nitrate.

TABLE XXI.—*Solubility of carbon dioxide in aqueous solutions of sodium nitrate at 15.2° C.*[a]

$NaNO_3$ per liter.	Solubility.	$NaNO_3$ per liter.	Solubility.
Grams.		*Grams.*	
89.3	0.835	208.4	0.621
104.2	.795	312.6	.495
125.0	.762	416.8	.385
156.3	.709	625.2	.244

[a] Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **34**, No. 3 (1886); Ann. Chim. Phys. (6), **25**, 226 (1892).

TABLE XXII.—*Solubility of carbon dioxide in aqueous solutions of sodium nitrate at various temperatures.*[a]

Solution.	Solubility at—		
	15.2° C.	18.38° C.	21.7° C.
17.02 per cent solution		0.822	0.551
28.36 per cent solution			.400
125.4 grams per liter (A)	0.747	.693	
100 c. c. (A) + 95.54 c. c. water	.876	.798	
100 c. c. (A) + 286.6 c. c. water	.946	.870	

[a] Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); **34**, No. 3 (1886).

Potassium nitrate.

TABLE XXIII.—*Solubility of carbon dioxide in aqueous solutions of potassium nitrate.*

Setschenow.[a]		Geffcken.[b]		
KNO_3 per liter.	Solubility at 15.2° C.	KNO_3 per liter.	Solubility at—	
			15° C.	25° C.
Grams.		*Grams.*		
58.8	0.959	54.24	1.001	0.7825
117.5	.8902	104.0	.943	.745
168.0	.825			
235.1	.781			

[a] Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); **35**, No. 7 (1887).
[b] Zeit. phys. Chem., **49**, 257 (1904).

In the first of the above papers Setschenow gives the solubility of carbon dioxide in 20.24 per cent solution of potassium nitrate as 0.641 at 22.4° C.

Ammonium nitrate.

TABLE XXIV.—*Solubility of carbon dioxide in aqueous solutions of ammonium nitrate at 15.2° C.*[a]

NH_4NO_3 per liter.	Solubility.	NH_4NO_3 per liter.	Solubility.
Grams.		*Grams.*	
2.8	1.013	101.0	0.962
5.6	1.010	202.1	.911
11.2	1.006	386.0	.819
22.5	.983	404.3	.807
55.0	.989	810.4	.612

[a] Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); Ann. Chim. Phys. (6), **25**, 226 (1892).

Ammonium sulphate.

The following figures give two determinations of Setschenow* on the solubility of carbon dioxide in ammonium sulphate solutions:

Grams $(NH_4)_2SO_4$ per liter	72.2	144.4
Solubility at 15.2° C	0.712	0.575

Sodium sulphate.

TABLE XXV.—*Solubility of carbon dioxide in aqueous solutions of sodium sulphate at 15.2° C.*[a]

Na_2SO_4 per liter.	Solubility.	Na_2SO_4 per liter.	Solubility.
Grams.		*Grams.*	
14.22	0.950	94.8	0.620
28.44	.876	142.2	.485
56.88	.753	284.4	.2335
71.10	.700	....	....

[a] Setschenow, Ann. Chim. Phys. (6), **25**, 226 (1892).

TABLE XXVI.—*Solubility of carbon dioxide in aqueous solutions of sodium sulphate at various temperatures.*[a]

Solution.	Solubility at—		
	15.2° C.	18.38° C.	21.7° C.
7.11 per cent solution	....	0.670	....
14.22 per cent solution	....	....	0.391
128.74 grams per liter (A)	0.472	.470	....
100 c. c. (A) +98.04 c. c. water	.771	.660	....
100 c. c. (A) +294.12 c. c. water	.850	.771	....

[a] Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); **34**, No. 3 (1886).

*Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875).

Potassium sulphocyanate.

TABLE XXVII.—*Solubility of carbon dioxide in aqueous solutions of potassium sulphocyanate at 15.2° C.*[a]

KSCN per liter.	Solubility.
Grams.	
326	0.691
489	.590
978	.387

[a] Setschenow. Ann. Chim. Phys. (6), **25**, 229 (1892).

Sodium chlorate.

TABLE XXVIII.—*Solubility of carbon dioxide in aqueous solutions of sodium chlorate at 15.2° C.*[a]

$NaClO_3$ per liter.	Solubility.
Grams.	
233.3	0.625
349.9	.506
699.8	.257

[a] Setschenow, Ann. Chim. Phys. (6), **25**, 229 (1892).

Calcium chloride.

TABLE XXIX.—*Solubility of carbon dioxide in aqueous solutions of calcium chloride at various temperatures.*[a]

Density.	$CaCl_2$ in solution.	Solubility at—			
		8° C.	16½° C.	22° C.	30° C.
	Per cent.				
1.0358	4.3650	0.9423	0.7587	0.6726	0.5957
1.0489	5.7390	.8548	.7260	.6159	.5266
1.0683	8.0453	.8383	.6740	.5809	.4998
1.1387	15.7925	.6315	.5202	.4709	.3945

[a] Mackenzie, Ann. Phys. Chem., **237**, 438 (1877).

Strontium chloride.

TABLE XXX.—*Solubility of carbon dioxide in aqueous solutions of strontium chloride at various temperatures.*[a]

Density.	$SrCl_2$ in solution.	Solubility at—			
		8° C.	16½° C.	22° C.	30° C.
	Per cent.				
1.0873	9.5108	0.7789	0.6633	0.5806	0.5079
1.1159	12.3248	.7367	.5859	.5071	.4386
1.1727	17.7132	.6057	.4727	.4435	.3672
1.3428	31.1937	.2854	.2449	.2474	.2231

[a] Mackenzie, Ann. Phys. Chem., **237**, 438 (1877).

Another determination by Setchenow* is that at 15.2° C. the solubility of carbon dioxide in 3.97 per cent strontium chloride solution is 0.893.

Barium chloride.

TABLE XXXI.—*Solubility of carbon dioxide in aqueous solutions of barium chloride at various temperatures.*[a]

Density.	$BaCl_2$ in solution.	Solubility at—			
		8° C.	16¼° C.	22° C.	30° C.
	Per cent.				
1.0684	7.3162	0.9694	0.7441	0.6803	0.5655
1.0916	9.7531	1.0207	.6445	.6072	.5426
1.1372	14.0297	....	.6179	.5235	.4672
1.2731	25.2146	.4949	.6179	.3833	.3152

[a] Mackenzie, Ann. Phys. Chem., **237**, 438 (1877).

Two determinations have been made by Setchenow,* as follows:

At 15.2° C. solubility in 5.2 per cent $BaCl_2$ solution is 0.894.

At 22° C. solubility in 6.94 per cent $BaCl_2$ solution is 0.670.

Magnesium sulphate.

TABLE XXXII.—*Solubility of carbon dioxide in aqueous solutions of magnesium sulphate at 15° to 16° C.*

$MgSO_4$ per liter.	Solubility.
Grams.	
26.5	0.901
40.0	.822
79.5	.669
159.0	.441
318.0	.188

[a] Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **35**, No. 7 (1887); Ann. Chim. Phys. (6), **25**, 226 (1892).

In Table XXXII the concentrations have been calculated from tables of the solubility of magnesium sulphate in water, as the original paper gave only the density of the concentrated solution, which was also saturated.

TABLE XXXIII.—*Solubility of carbon dioxide in aqueous solutions of magnesium sulphate at various temperatures.*[a]

Composition of solution.	Temperature.	Solubility.
	°C.	
8.432 grams $MgSO_4$+500 grams water	26.00	0.712
33.73 grams $MgSO_4$+500 grams water	25.00	.586
60.2 grams $MgSO_4$+500 grams water	18.38	.523
15.05 per cent solution	22.40	.310

[a] Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); Ann. Chim. Phys. (6), **25**, 225 (1892).

*Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875).

Zinc sulphate.

TABLE XXXIV.—*Solubility of carbon dioxide in aqueous solutions of zinc sulphate at 15° to 16° C.*[a]

$ZnSO_4$ per liter.	Solubility.
Grams.	
38.3	0.903
76.7	.783
230.0	.474
460.0	.209

[a] Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **35**, No. 7 (1887); Ann. Chim. Phys. (6), **25**, 226 (1892).

In Table XXXIV the concentrations have been calculated from tables of the solubility of zinc sulphate in water, as the original papers gave only the density of the most concentrated solution, which was also saturated.

TABLE XXXV.—*Solubility of carbon dioxide in aqueous solutions of zinc sulphate at various temperatures.*[a]

Composition of solution.	Temperature.	Solubility.
	° C.	
9.84 grams $ZnSO_4$ + 500 grams water	26.00	0.715
39.34 grams $ZnSO_4$ + 500 grams water	25.00	.593
80.7 grams $ZnSO_4$ + 500 grams water	18.38	.522

[a] Setschenow, Mémoires de l'acad. impér. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875); Ann. Chim. Phys. (6), **25**, 226 (1892).

Other salts.

TABLE XXXVI.—*Solubility of carbon dioxide in aqueous solutions of different salts.*[a]

Composition of solution.	Temperature.	Solubility.
	° C.	
6.27 per cent $Ba(NO_3)_2$ solution	15.2	0.922
8.35 per cent $Ba(NO_3)_2$ solution	22.0	.715
4.10 per cent $Ca(NO_3)_2$ solution	15.2	.923
5.29 per cent $Sr(NO_3)_2$ solution	15.2	.916
12.8 per cent $CaSO_4$ solution	18.38	.672
34 per cent $AgNO_3$ solution	18.38	.648
11.9 per cent $MgCl_2$ solution	22.4	.451

[a] Setschenow, Mémoires de l'acad. imper. des sci. de St.-Pétersb. (7), **22**, No. 6 (1875).

GENERAL CONCLUSIONS.

The following general conclusions may be drawn from the work upon the solubility of carbon dioxide in various solutions:

1. The solubility in salt solutions is less than in an equal volume of water.

2. The solubility of carbon dioxide in water is increased by addition of nitric acid.

3. The solubility of carbon dioxide in sulphuric acid is decreased by the addition of water; likewise the solubility of carbon dioxide

in water is decreased by the addition of sulphuric acid; consequently there is a mixture of sulphuric acid and water, which dissolves a minimum quantity of carbon dioxide.

4. The more concentrated the solutions are, the less carbon dioxide is absorbed.

5. The solubility in solutions of strontium chloride is between that in calcium and barium chlorides.

6. The quantity of carbon dioxide absorbed becomes less as the temperature increases.

7. The solubility is less in sulphate solutions than in chloride solutions, and less in chloride solutions than in nitrate solutions.

8. Solutions of sodium salts absorb carbon dioxide less readily than solutions of similar potassium salts, and solutions of ammonium salts are better solvents than solutions of either sodium or potassium salts.

LIME.

SOLUBILITY OF LIME IN WATER.

Many experimenters have investigated the solubility of lime in water at different temperatures, and on account of the many precautions which must be taken in such determinations the results have not shown a satisfactory agreement. It is essential that the water in which the lime is to be dissolved should be absolutely free from impurities, especially materials of organic origin, which will be shown to possess a very great solvent action on lime. It is also essential in any accurate determinations that the source and impurities of the lime should be known. That there is a difference in the solubility of lime, depending on the source and consequently upon the impurities present, is seen from the determinations of Lamy[a] upon lime obtained from different sources. These results are given in the following table:

TABLE XXXVII.—*Solubility of lime obtained from different sources.*

Temperature.	Lime in 1,000 parts of solution.		
	From nitrate.	From marble.	Hydrate.
° C.	*Parts.*	*Parts.*	*Parts.*
0	1.362	1.381	1.430
10	1.311	1.342	1.384
15	1.277	1.299	1.344
30	1.142	1.162	1.195
45	.996	1.005	1.033
60	.864	.868	.885
100	.562	.576	.584

[a] Compt. rend., **86**, 333 (1878).

The solubility of lime in water at different temperatures has been investigated by many experimenters [a] and the results of these investigations have been collected in the following table and the accompanying plate:

TABLE XXXVIII.—*Solubility of lime (CaO) in water.*

[Given in grams per liter.]

Temp.	Dalton.	Phillips.	Carles.	Pavesi and Rotondi.	Wittstein.	Tichborne.	Maben.
°C.							
0							1.318
5							1.309
10							1.298
13				1.274			
15							1,284
15.6	1.29	1.29			1.37	1.35	
19			1.251	1.241			
20							1.264
23				1.228			
25							1.203
30							1,160
35							1,100
40							1.073
45							1.015
50							.982
54.4	1.03						
55							.906
60							.880
65							.828
70							.810
75							.763
80							.734
85							.720
90							.633
95							.606
99							
100	.789				.752	.747	.606
109						.560	
120							
150							
190							

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[a] Dalton, New System of Chemical Philosophy, Manchester (1808), cited by Phillips, Ann. Chim. Phys. (2), **16**, 213 (1821); Carles, Pharm. Jour. Trans. (3), **4**, 550 (1874); Pavesi and Rotondi, Ber. deutsch. chem. Ges., **7**, 817(1874); Wittstein, Repert. Pharm. (3), **1**, 182 (1848); Boutron and Boudet, Jour. Pharm. (3), **26**, 16 (1854); Tichborne, Chem. News, **24**, 199 (1871); Maben, Pharm. Jour. Trans. (3), **14**, 505 (1883); Lunge, Jour. Soc. Chem. Ind., **11**, 882 (1892); Cabot, ibid., **16**, 417 (1897); Herzfeld, Bied. Centr., **27**, 571 (1898); Guthrie, Jour. Soc. Chem. Ind., **20**, 223 (1901); Herold, Zeit. Elektrochem., **11**, 417 (1905); Tilden and Shenstone, Proc. Roy. Soc., **38**, 33 (1885).

TABLE XXXVIII.—*Solubility of lime (CaO) in water*—Continued.

[Given in grams per liter.]

Temp.	Lunge.	Cabot.	Herzfeld.	Guthrie.	Herold.	Tilden and Shenstone.
°*C.*						
0	...	1.36	...	...	...	...
5	...	...	...	1.350	...	...
10	...	...	...	1.342	...	...
13	...	...	...	...	...	...
15	...	1.31	1.29	1.320	...	...
15.6	...	...	...	...	...	...
19	...	...	...	...	...	1.182
20	1.374	...	1.23	1.293	...	...
23	...	...	...	...	...	...
25	...	...	1.18	1.254	...	...
30	...	...	1.13	1.219	...	...
35	...	...	1.08	1.161	...	...
40	1.162	...	1.04	1.119	...	...
45	...	...	.996	...	...	...
50	...	...	.958	.981	...	...
54.4	...	...	...	...	...	...
55	...	...	.902	...	...	...
60	1.026	...	.864	.879	...	...
65	...	...	.801	...	...	...
70	...	...	.752	.781	...	...
75	...	...	.709	...	...	...
80	.845	...	.675	.740	...	...
85	...	...	...	...	...	...
90	...	...	...	.696	...	...
95	...	...	...	...	...	...
99	...	.635	...	...	...	...
100	.664	...	...	.597	...	...
109	...	...	...	...	...	...
120	...	...	...	...	0.305	...
150	...	...	...	...	.169	.246
190	...	...	...	...	.084	...

In spite of the lack of satisfactory accord between these various determinations, the results indicate that lime is about twice as soluble[a] at 0° as it is at 100° C., and that the solubility curve approximates a straight line between the temperatures 25° and 100° C. (See figure 1.)

SOLUBILITY OF LIME IN AQUEOUS SOLUTIONS.

Ammonium chloride.

There are many qualitative statements in the literature that lime is much more soluble in ammonium chloride solutions than in water. The quantitative results obtained by Noyes and Chapin[b] are given in the following table:

TABLE XXXIX.—*Solubility of lime in ammonium chloride solutions at 25° C.*

Ammonium chloride per liter.	Lime per liter.
Grams.	*Grams.*
0.0	1.134
1.164	1.631
2.328	2.201
4.655	3.348

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[a] This result is also given by Goldammer, Pharm. Centr., **26**, 442, 455 (1885); abstr. in Jour. Soc. Chem. Ind., **5**, 450 (1866).

[b] Zeit. phys. Chem., **28**, 518 (1899).

From this table it will be seen that by increasing the quantity of ammonium chloride in the solution the solubility of lime is also increased, and at the concentrations employed the increase is nearly proportional to the concentration of ammonium chloride.

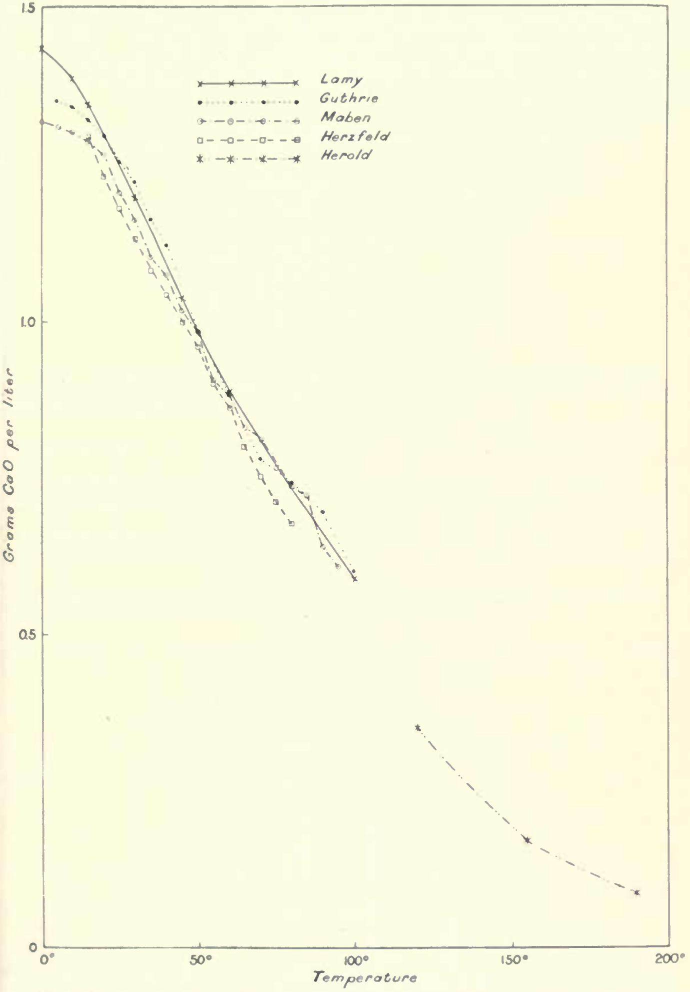

Fig. 1.—Solubility of lime in water at various temperatures according to various experiments.

Sodium chloride.

Lime is more soluble in sodium chloride solutions than in pure water. According to Lunge,[a] at 50° C. a sodium chloride solution (5 to 10 per cent) dissolves about 35 per cent more lime than does water at the same temperature. The solubility for different concentrations of sodium chloride at different temperatures has been given by Cabot[b] as follows:

Table XL.—*Solubility of lime in sodium chloride solutions.*

NaCl per liter.	CaO per liter.		
	0° C.	15° C.	99° C.
Grams.	*Grams.*	*Grams.*	*Grams.*
0	1.36	1.31	0.635
30	1.813	1.703	.969
60	....	1.824	1.004
120	1.86	1.722	1.015
240	1.36	1.274	.771
Saturated.	1.054	.929	.583

With increase of sodium chloride in solution the solubility of lime increases to a maximum and then decreases again until the saturation point for sodium chloride is reached.

These results are confirmed by the experiments of Maigret[c] upon the solubility of lime in sodium chloride solutions. The results also show that the presence of sodium hydroxide causes a decrease in the quantity of lime in solution. The following table gives the results of this work:

Table XLI.—*Solubility of lime in sodium chloride solutions containing various quantities of sodium hydroxide.*

NaCl per liter.	CaO per liter.		
	No NaOH.	0.8 gram NaOH per liter.	4.0 grams NaOH per liter.
Grams.	*Grams.*	*Grams.*	*Gram.*
0	1.3	0.8	0.22
5	1.4	.9	....
10	1.6	1.0	....
25	1.7	1.1	....
50	1.8	1.25	....
75	1.9	1.4	.55
100	1.85	1.4	....
125	1.7	1.3	....
150	1.65	1.25	.44
175	1.6	1.2	....
182	1.6	1.2	....
200	1.55	1.1	....
225	1.4	1.0	....
250	1.3	.9	....
275	1.2	.7	....
300	1.1	.7	.22
314	1.0	....	....

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[a] Jour. Soc. Chem. Ind., **11**, 882 (1892).

[b] Jour. Soc. Chem. Ind., **16**, 417 (1897).

[c] Bul. Soc. Chim. (3), **33**, 631 (1905).

Potassium chloride.

According to Lunge,[a] at 50° C. a potassium chloride solution (5 to 10 per cent) dissolves about 35 per cent more lime than does water at the same temperature. The solubility for different concentrations of potassium chloride at different temperatures has been given by Cabot[b] as follows:

TABLE XLII.—*Solubility of lime in potassium chloride solutions.*

KCl per liter.	CaO per liter.		
	0° C.	15° C.	99° C.
Grams.	*Grams.*	*Grams.*	*Gram.*
0	1.36	1.31	0.635
30	1.701	1.658	.788
60	1.725	1.674	.876
120	1.718	1.606	.894
240	1.248	1.199	.612
Saturated.	1.21	....	....

The solubility increases with increase of potassium chloride to a maximum and then decreases again as the concentration of potassium chloride approaches the saturation point.

Calcium chloride.

It might be expected that the solubility of lime in the solution of a salt yielding a common ion would be depressed. There are indications that this actually happens at lower temperatures and in the more dilute solutions of calcium chloride. In the more concentrated solutions, however, this solubility is augmented, as will be observed from the following table by Lunge[b] and Zahorsky.[c]

TABLE XLIII.—*Lime dissolved at different temperatures by various solutions of calcium chloride.*

$CaCl_2$	CaO per 100 c. c. solution.				
	20° C.	40° C.	60° C.	80° C.	100° C.
Per cent.	*Gram.*	*Gram.*	*Gram.*	*Gram.*	*Gram.*
0	0.1374	0.1162	0.1026	0.0845	0.0664
5	.1370	.1160	.1020	.0936	.0906
10	.1661	.1419	.1313	.1326	.1389
15	.1993	.1781	.1706	.1736	.1842
20	[a] .1857	.2249	.2204	.2295	.2325
25	[a] .1661	[a] .3020	.2989	.3261	.3710
30	[a] .1630	[a] .3684	.3664	.4122	.4922

[a] Oxychloride separated out.

Lunge has pointed out from these results that solutions up to 10 per cent calcium chloride at ordinary or slightly raised temperatures alter the solubility very little from that in pure water. At the higher temperatures the presence of calcium chloride increases the solubility of lime proportionately with the quantity of calcium chloride, except where the phenomenon is complicated by precipitation of the solid oxychloride. The changes in solubility due to changes of temperature are not so great as the changes consequent upon changes in concentration of calcium chloride.

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[a] Jour. Soc. Chem. Ind., **11**, 882 (1892).

[b] Jour. Soc. Chem. Ind., **16**, 417 (1897).

[c] Zeit. anorg. Chem., **3**, 34 (1893).

The recovery of manganese peroxide in the Weldon process is brought about by the action of lime upon the manganous salts. The presence of considerable quantities of calcium chloride is essential, and according to Lunge the most natural explanation is that it serves as a solvent for lime, as lime is much more soluble in hot solutions of calcium chloride than in water. This increased solubility has been attributed to the formation of an oxychloride in solution. That this explanation is not sufficient follows from a consideration of the relative solubilities of the oxychloride and of lime. Of two substances which may separate out as solid phase under any conditions the stable solid is that one whose solubility in the liquid is least, or which, after the precipitation has taken place, leaves the solution least concentrated. As the oxychloride separates out at the higher concentrations, it follows that the content of free lime in the solution is less than if the solid phase had been calcium hydroxide. The increased solubility of lime in calcium chloride solutions of the higher concentrations can not therefore be satisfactorily explained on the ground of the formation of oxychloride in solution.

The crystalline precipitate obtained by heating lime in a concentrated solution of calcium chloride was first observed by Buchholtz[a] and later by Tromsdorf.[a] At first it was supposed to be a modification of lime, but Berthollet[a] subsequently showed it to be a compound of lime with calcium chloride. The ratio of lime to calcium chloride has been definitely determined by many experimenters as three to one, but the number of molecules of water of crystallization has been variously determined. Rose,[b] Ditte,[c] and André[d] have ascribed to it the formula $3CaO.CaCl_2.16H_2O$; Beesley[e] has given it the formula $3CaO.CaCl_2.14H_2O$; while Rose,[f] Precht,[g] Grimshaw,[h] and Zahorsky[i] indicate the formula $3CaO.CaCl_2.15H_2O$.

This compound is formed in large quantities in the production of ammonia by the action of lime on ammonium chloride, and all the above work upon its composition has been upon the compound obtained by dissolving lime in warm or hot concentrated calcium chloride solutions and allowing it to settle after filtration. Upon standing, large crystals of the oxychloride separate. These are decomposed by water and by alcohol. Ditte has shown that when the oxychloride is treated with water the solution contains all the calcium chloride and part of the lime, while the residue of lime remains as a fine powder. This decomposition does not take place at 10° C. after the solution has reached the concentration of 85 grams calcium chloride per liter. Alcohol acts similarly, and at 17° C. no decomposition occurs if the alcohol contains 130 grams calcium chloride per liter, but calcium oxychloride passes into solution unchanged. Zahorsky has also proved that sodium, potassium, and ammonium chlorides in solution all decompose the oxychloride of calcium, free lime being left as a fine powder. Glycerol, however, has no decomposing influence upon the oxychloride, but dissolves it readily in the cold, the solution undergoing no decomposition upon heating. When an equal volume of water is added to the solution in glycerol, decomposition takes place, lime separating.

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[a] See Berthollet, Essai de Statique Chimique, **1**, 350.

[b] Schweig, Jour., **29**, 155 (1820).

[c] Compt. rend., **91**, 576 (1880).

[d] Compt. rend., **92**, 1452 (1881); Ann. Chim. Phys. (6), **3**, 66 (1884).

[e] Phar. Jour. Trans., **9**, 568 (1850).

[f] Schweig. Jour., **29**, 155 (1820).

[g] See Zahorsky, Zeit. anorg. Chem., **3**, 34 (1893).

[h] Chem. News, **30**, 280 (1874).

[i] Zeit. anorg. Chem., **3**, 34 (1893).

Sodium and potassium hydroxides.

According to Pelouze[a] 100 parts of a solution containing 1 part of sodium or potassium hydroxide dissolves not more than one fifty-thousandth of 1 part of lime.

The following results by d'Anselme[b] prove that the solubility of lime in sodium hydroxide solutions decreases with increasing concentrations of the caustic alkali and also with rise in temperature:

TABLE XLIV.—*Solubility of lime in solutions of sodium hydroxide.*

NaOH per liter.	CaO per liter.			
	20° C.	50° C.	70° C.	100° C.
Grams.	*Grams.*	*Gram.*	*Gram.*	*Gram.*
0.0	1.17	0.88	0.75	0.54
0.4	.94	.65	.53	.35
1.6	.57	.35	.225	.14
2.67	.39	.20	.11	.05
5.0	.18	.06	.04	.01
8.0	.11	.02	.01	Traces.
20.0	.02	Traces.	.00	.00

[a] Ann. Chim. Phys. (3), **33**, 5 (1851).

[b] Bul. Soc. Chim. (3), **29**, 936 (1903).

Calcium sulphate.

The mutual solubility of gypsum in lime solutions and of calcium hydroxide in gypsum solutions has recently been determined at 25° C. in this laboratory by Cameron and Bell[a] with the following results:

TABLE XLV.—*Mutual solubility of gypsum and lime at 25° C.*

$CaSO_4$ per liter.	CaO per liter.	Solid phase.
Grams.	*Grams.*	
0.000	1.166	$Ca(OH)_2$.
.391	1.141	$Ca(OH)_2$.
.666	1.150	$Ca(OH)_2$.
.955	1.215	$Ca(OH)_2$.
1.214	1.212	$Ca(OH)_2$.
1.588	1.222	$Ca(OH)_2$. $CaSO_4.2H_2O$.
1.634	.939	$CaSO_4.2H_2O$.
1.722	.611	$CaSO_4.2H_2O$.
1.853	.349	$CaSO_4.2H_2O$.
1.918	.176	$CaSO_4.2H_2O$.
2.032	.062	$CaSO_4.2H_2O$.
2.126	.000	$CaSO_4.2H_2O$.

It will be seen from these results that with increasing lime content in the solution the solubility of gypsum is steadily depressed. With increasing amounts of gypsum in the solution the solubility of lime seems to be nearly the same as in pure water. These results have been recently confirmed by further work in this laboratory by Bell and Taber.

Calcium nitrate.

The following table by Cameron and Robinson[b] gives the content of free lime in various solutions of calcium nitrate at 25°.

TABLE XLVI.—*Solubility of lime in calcium nitrate solutions at 25°.*

Density $\frac{25°}{25°}$.	CaO as $Ca(OH)_2$.		$Ca(NO_3)_2$.	
	In 100 c. c.	In 100 grams H_2O.	In 100 c. c.	In 100 grams H_2O.
Grams.	*Gram.*	*Gram.*	*Grams.*	*Grams.*
1.0249	0.095	0.096	3.35	3.38
1.0484	.105	.109	8.18	8.52
1.0940	.120	.125	12.91	13.42
1.1383	.170	.181	19.43	20.73
1.1840	.171	.187	26.49	28.98
1.2101	.180	.198	29.82	32.84
1.2287	.190	.212	32.97	36.83
1.2290	.191	.213	33.27	37.55
1.2541	.200	.224	35.87	40.25
1.2581	.203	.230	37.04	41.98
1.2826	.226	.260	40.88	47.00
1.2905	.229	.263	41.08	47.16
1.3337	.277	.332	48.99	58.67
1.3735	.346	.429	50.88	69.40
1.4195	.440	.545	63.93	83.03
1.4840	.331	.449	73.58	99.70
1.5330	.263	.371	81.91	115.50
1.5809	.203	.303	90.38	135.30
1.5842	.000	.000	91.84	139.30

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[a] Jour. Am. Chem. Soc., **28**, 1220 (1906); Bul. No. 33, Bureau of Soils, U. S. Dept. Agr. (1906).
[b] Jour. Phys. Chem., **11**, 273 (1907).

These results are plotted in the accompanying diagram (fig. 2), in which four distinct curves are seen. In order to determine the composition of the solid phases along each of these curves the triangular diagram method of Schreinemakers and Bancroft was employed, and the following table gives the composition of the soluions and of the corresponding solid phases with adhering mother iquor.

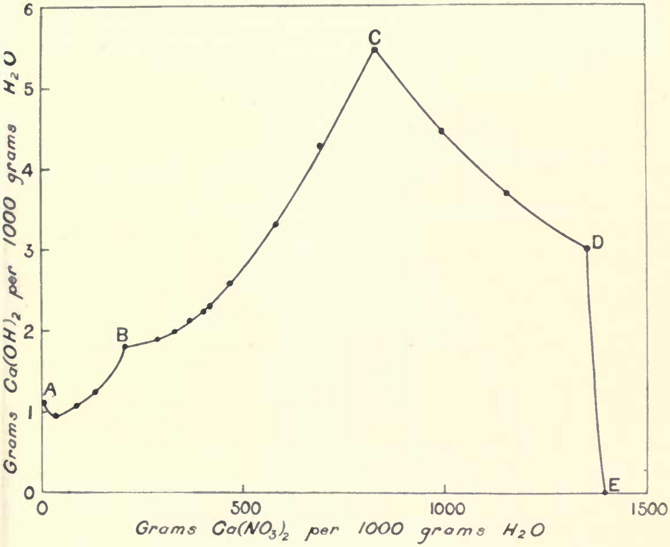

FIG. 2.—Solubility of lime in solutions of calcium nitrate at 25° C.

TABLE XLVII.—*Composition of solutions and solid residues at 25°.*

Point.	Solution.		Point.	Precipitate with adhering solution.	
	CaO.	N_2O_5.		CaO.	N_2O_5.
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
F	1.21	2.15	F′	40.85	1.00
G	4.16	7.80	G′	37.70	4.09
H	7.77	14.70	H′	33.26	7.20
I	9.34	17.84	I′	29.73	9.87
J	9.83	18.77	J′	27.49	11.60
K	14.21	26.87	K′	38.59	15.71
L	17.20	33.32	L′	31.64	36.36
M	18.56	35.33	M′	31.72	37.21

From the diagram (figure 3) it will be seen that the extension of the lines F F′ and G G′ meet in a point corresponding to solid calcium hydroxide. This substance, therefore, was the solid phase in contact with the solutions represented by the curve A B.

It is evident that the lines joining the points representing the composition of the solutions and their corresponding precipitates for the second branch of the curve, when extended, do not meet at a common point. The precipitate is therefore of variable composition, and since there can be only one solid phase present, it must be a series of solid solutions containing calcium oxide, nitric oxide, and probably water.

The residues along the third branch of the curve proved to be a substance occurring in long acicular crystals. As scaled off from the diagram its percentage composition is CaO, 39.5; N_2O_5, 38.0, and H_2O, 22.5; corresponding to the compound $2CaO.N_2O_5.3\frac{1}{2}H_2O$, and is identical with the one described by Werner.[a]

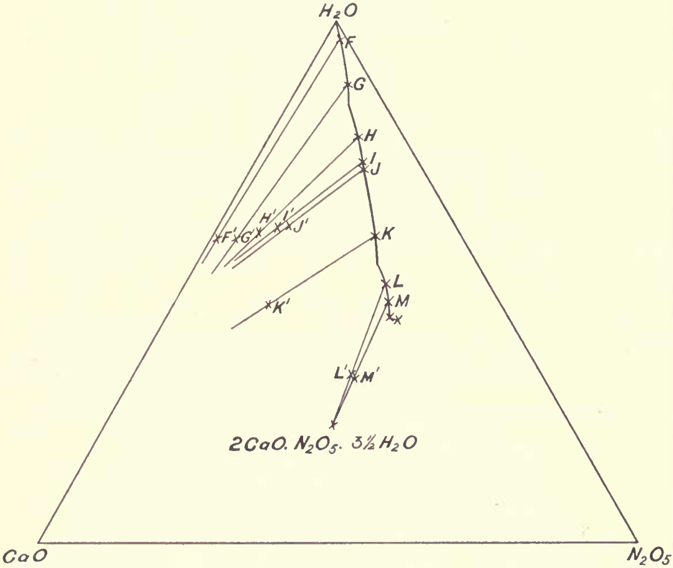

FIG. 3.—Triangular diagram showing the composition of the solutions and of the solid phases in contact with the solutions at 25° C., where there are present lime, calcium nitrate, and water.

The solid phase in contact with the solutions along the fourth branch of the curve was undoubtedly the well-known normal nitrate $Ca(NO_3)_2.4H_2O$, and no further attempt was made to demonstrate its composition. The data for the "constant" solutions have been brought together in the following table:

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[a] Ann. Chim. Phys. (6), **27**, 570 (1892); Compt. rend., **115**, 169 (1892).

TABLE XLVIII.—*Data for the "constant" solutions in the system, calcium nitrate, lime, and water at 25° C.*

Points	Solid phases in contact with solution	Concentration of respective solutions; grams per 100 grams H_2O.	
		CaO as $Ca(OH)_2$	$Ca(NO_3)_2$
A	$Ca(OH)_2$	0.118	0.0
B	$Ca(OH)_2$, and solid solution $(CaO.xN_2O_5.yH_2O)$	.170	20.73
C	Solid solution $(CaO.xN_2O_5.yH_2O)$ and $CaO.N_2O_5.3\frac{1}{2}H_2O$	.140	83.03
D	$CaO.N_2O_5.3\frac{1}{2}H_2O$, and $Ca(NO_3)_2.4H_2O$	.203	135.3
E	$Ca(NO_3)_2.4H_2O$	.000	139.30

Glycerol.

The following table gives the results of Berthelot[a] upon the solubility of lime in glycerol solutions.

TABLE XLIX.—*Solubility of lime in glycerol solutions at 5° C.*

Glycerol per 100 c. c. solution.	CaO per 100 c. c. solution.
Grams.	*Gram.*
1	0.165
2	.186
2.50	.192
2.86	.196
5	.240
10	.370

The results of Carles[b] are in accord with these, showing that as the content of the solution in glycerol becomes greater, the solubility of lime also increases.

TABLE L.—*Solubility of lime in glycerol solutions.*

Solution containing		CaO dissolved.
Water.	Glycerol.	
Grams.	*Grams.*	*Grams.*
1,000	0	1.251
1,000	50	1.865
1,000	100	2.583
1,000	200	4.040
1,000	400	6.569

The presence of glycerol in solution increases the solubility of lime, as the following table by Puls[c] indicates:

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[a] Ann. Chim. Phys. (3), **46**, 173 (1856). [b] Pharm. Jour. Trans. (3), **4**, 550 (1874).
[c] Jour. prakt. Chem., **123**, 83 (1877).

TABLE LI.—*Solubility of lime in glycerol solutions.*

Glycerol per 100 grams solution.	CaO per 100 grams solution.	Glycerol per 100 grams solution.	CaO per 100 grams solution.
Grams.	*Gram.*	*Grams.*	*Grams.*
0.0	0.148	10.00	0.370
2.00	.186	26.97	.595
2.50	.192	37.91	.852
2.86	.196	51.15	1.434
5.00	.240		

The following table contains the results of Herz and Knoch:[a]

TABLE LII.—*Solubility of lime in glycerol solutions at 25° C.*

Density $\frac{25^\circ}{25^\circ}$	Glycerol in solvent.	$Ca(OH)_2$ per liter.
	Per cent.	*Grams.*
1.0003	0.0	1.59
1.0244	7.15	3.01
1.0537	20.44	4.51
1.0842	31.55	8.33
1.1137	40.95	14.80
1.1356	48.70	16.30
1.2072	69.20	35.40

Mannite.

In mannite solutions also Berthelot[b] has found that the solubility of lime is increased. The results are given in the following table:

TABLE LIII.—*Solubility of lime in mannite solutions at 5° C.*

Mannite per 100 c. c. solution.	CaO per 100 c. c. solution.	Mannite per 100 c. c. solution.	CaO per 100 c. c. solution.
Grams.	*Gram.*	*Grams.*	*Gram.*
0.0	0.148	1.37	0.194
.096	.154	1.60	.207
.192	.155	1.92	.225
.96	.186	2.40	.255
1.09	.190	4.80	.372
1.20	.193	9.60	.753

Sugar.

The use of lime to neutralize the acid employed in the settling tanks in sugar factories makes the subject of the solubility of lime in sugar solutions one of prime importance. Considerable work has been done on this subject and the results are not altogether concordant. Owing to the fact that sugar and lime form addition compounds the quantity of lime added to a given sugar solution should be taken into account, as the solid phase resulting contains considerable percentages of sugar. Several formulas have been ascribed to the double compound obtained by adding lime to sugar solutions at ordinary temperature. Péligot,[c] Soubeiran,[d] and Benedikt[e] have recorded the compound $C_{12}H_{22}O_{11}.CaO$; Soubeiran found another compound, $2C_{12}H_{22}O_{11}.3CaO$; and Péligot[a] and Dubrunfaut[b] have recorded the compound $C_{12}H_{22}O_{11}.3CaO$. The last author has also determined the ratio of lime to sugar in saturated solutions at different temperatures. The molecular ratio of lime to sugar is eight times as great at or below 0° as it is at 100° C. Péligot[c] has determined the composition of the solid phase in contact with a series of solutions in which the sugar content varies from 2.5 to 40 grams of sugar per 100 grams of water The composition of the solid phase was found to vary continuously from 13.8 per cent to 21.0 per cent lime, thus indicating that lime and sugar form a series of solid solutions, of which the above recorded "compounds" are members. The so-called solubility of lime in sugar solutions is in fact, then, the quantity of lime in the sugar solution, the solid phase being one of the above described solid solutions. When these solids are heated with water the solutions cloud, as the quantity of lime in hot sugar solutions is very much less than in cold solutions. On cooling again the solutions clear up. The following results of Lamy[d] show this to be the case in 10 per cent sugar solutions. The solubility in water at the same temperature has been given, and it will be seen that sugar increases the solubility much more in cold solutions than it does when the solutions are hot.

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[a] Zeit. anorg. Chem., **46,** 193 (1905).

[b] Ann. Chim. Phys. (3), **46,** 173 (1856).

[c] Ann. Chim. Phys. (2), **67,** 113 (1838); Compt. rend., **32,** 333 (1851).

[d] Jour. Pharm. (3), **1,** 469 (1842).

[e] Ber. deutsch. chem. Ges., **6,** 413 (1873).

TABLE LIV.—*Solubility of lime in water and in 10 per cent sugar solutions.*

Temperature.	CaO per 1,000 grams 10 per cent sugar solution.	CaO per 1,000 grams water.
° C.	*Grams.*	*Grams.*
100	15.5	6.0
70	23.0	7.9
50	53.0	9.6
30	120.5	11.7

In the following table there have been recorded the results of Berthelot[e] upon the solubility of lime in various sugar solutions:

TABLE LV.—*Solubility of lime in sugar solutions at 5° C.*

Sugar per 100 c. c. solution.	CaO per 100 c. c. solution.	Sugar per 100 c. c. solution.	CaO per 100 c. c. solution.
Grams.	*Gram.*	*Grams.*	*Grams.*
0.0	0.148	1.200	.316
.096	.154	1.386	.326
.191	.172	1.660	.364
.400	.194	2.000	.433
.960	.264	2.401	.484
1.058	.281	4.850	1.031

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[a] Jour. Pharm. (3), **19**, 324 (1851).

[b] Compt. rend., **32**, 498 (1851).

[c] Compt. rend., **32**, 333 (1851).

[d] See Weisberg. Bul. Soc. Chim. (3), **23**, 740 (1900).

[e] Ann. Chim. Phys. (3), **46**, 173 (1856).

Weisberg[a] has collected the data of several authors upon the solubility of lime in sugar solutions and has calculated the ratio of lime to sugar in the solution. Also in the following table are the results obtained by using different quantities of lime with which to saturate the solutions. In all probability the quantity of lime has caused a marked change in the quantity of sugar in the solution by the union of lime and sugar in the solid phase.

TABLE LVI.—*Solubility of lime in sugar solutions according to various authors.*

Berthelot.		Péligot.		Petit.		Schatten.	
Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.
Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*
0.400	48.50	2.33	16.00	1.71	16.4	1	29.10
.960	27.48	4.64	18.06	3.52	16.4	2	22.70
1.058	26.57	6.97	20.33	4.275	16.4	3	20.95.
1.386	23.52	9.31	22.10	6.84	18.4	6	19.66
1.660	21.92	11.39	22.40	8.55	20.5	8	20.64
2.000	21.65	13.47	22.70	10.40	25.3	11	23.17
2.401	20.16	15.55	23.00	17.10	25.7	13	24.23
4.850	21.15	17.63	23.15	22.80	27.3	16	26.26
....	....	21.32	24.69	....	....	....	....

TABLE LVII.—*Solubility of lime in sugar solutions according to Weisberg, showing the effect of adding lime in varying quantities.*

[T=16° C.]

CaO in excess.		CaO in great excess.	
Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.
Grams.	*Grams.*	*Grams.*	*Grams.*
0.7814	37.9	0.625	71.6
.912	32.3	.964	53.4
1.400	30.5	2.084	36.0
1.693	28.9	3.028	32.3
4.754	27.7	3.451	31.7
5.73	27.1	4.168	30.2
10.59	27.5	4.880	28.7
11.20	27.2	5.73	28.3
12.50	27.3	6.12	27.4
13.93	27.9	6.25	27.7
14.49	27.5	6.51	27.5
16.41	28.0	7.55	27.9
....	....	8.20	27.3

The following table by Weisberg[b] shows the different solubility of quicklime, of calcium hydroxide, and of slaked lime. The apparent difference may probably be ascribed to the nonattainment of equilibrium conditions.

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[a] Bul. Soc. Chim. (3), **21,** 773 (1899).

[b] Bul. Soc. Chim. (3), **23,** 740 (1900).

TABLE LVIII.—*Solubility of quicklime and of slaked lime in sugar solutions at 15° to 16° C.*

CaO.		$Ca(OH)_2$.		$Ca(OH)_2+H_2O$.	
Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.
Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*
13.00	27.75	13.00	25.40	....	....
11.34	27.57	11.96	25.45	11.18	22.40
10.30	27.87	10.87	25.40	10.40	22.90
9.67	27.61	9.67	25.00	....	....
8.27	27.49	8.90	24.74	8.68	22.80
7.64	27.50	8.06	24.72	7.28	21.70
6.84	27.42	6.97	24.50	6.29	20.90
5.77	27.80	5.46	24.50	5.22	20.55
4.73	27.90	4.52	24.23	4.03	20.60
3.95	27.73	3.56	23.60	....	....
3.02	27.78	2.57	23.40	....	....
2.29	27.93	1.85	23.30	2.91	20.05

Finally, Weisberg has compared the solvent action of hot sugar solutions on lime with that of cold sugar solutions.

TABLE LIX.—*Solubility of various samples of lime in hot and cold sugar solutions.*

CaO.				$Ca(OH)_2$.				$Ca(OH)_2+H_2O$.			
Ordinary temperature.		80° C.		Ordinary temperature.		90° C.		Ordinary temperature.		90° C.	
Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.	Sugar per 100 c. c. solution.	CaO per 100 grams sugar.
Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*
13.68	27.8	10.97	21.18	12.13	25.5	8.16	7.50	....	....	....	....
10.76	27.6	7.49	16.60	11.59	26.0	7.12	6.84	11.49	23.1	8.79	11.78
6.56	27.7	4.58	16.15	9.15	26.0	5.72	6.36	8.85	23.1	6.29	8.18
4.00	27.4	2.68	13.59	8.68	25.5	5.62	7.67	5.67	23.1	3.95	7.65
4.43	27.8	2.78	8.85	....	....	....	....	....	....	....	....

GENERAL CONCLUSIONS.

1. The apparent solubility of lime in aqueous solutions is greatly dependent on its origin, and therefore on the impurities it contains.

2. The solubility of lime at 0° C. is approximately twice its solubility at 100° C. The temperature-solubility curve approximates a straight line.

3. The solubility of lime in dilute solutions of the chlorides of sodium, potassium, and ammonium is greater than in pure water. The solubility curves for solutions of the chlorides of sodium and potassium have maximum points, and in saturated solutions the solubility is less than in pure water.

4. The solubility of lime in very dilute solutions of calcium chloride seems to be less than in pure water, but as the concentration increases the solubility is raised much above that in pure water, especially at higher temperatures.

5. At lower temperatures and in the more concentrated solutions of calcium chloride the stable solid phase is calcium oxychloride.

6. The presence of other hydroxides depresses markedly the solubility of lime.

7. The presence of gypsum does not appreciably affect the solubility of lime.

8. In contact with very dilute solutions of calcium nitrate, lime passes into solution as such, the solubility increasing with concentration of nitrate; at higher concentrations the stable solid is one of a series of solid solutions, the content of lime still increasing with increase of nitrate; at still higher concentrations the stable solid is a basic nitrate of definite composition, and the concentration of lime in solution falls with increase of nitrate; finally, at very high concentrations the neutral nitrate separates as a solid phase.

9. In solutions of glycerol or mannite the solubility of lime is increased markedly with increase of concentration of the carbohydrate.

10. When lime is brought into contact with sugar solutions the ratio of lime to sugar in the solid varies continuously with the composition of the solution, and consequently the solid compound resulting when lime is added in excess to a sugar solution is one of a series of solid solutions.

11. Cold sugar solutions have a much greater solvent action upon lime than have the same solutions when hot. Heating tends to precipitate one of the solid solutions described above.

12. The ratio of lime to sugar in solution depends on the temperature and on the concentration.

CALCIUM CARBONATE.

MODIFICATIONS OF CALCIUM CARBONATE.

The formation of carbonates in nature has been the subject of much research by chemical geologists.[a] Two forms of calcium carbonate are common, calcite and aragonite, and there seems to be good reason for believing that at the higher temperatures and in salt solutions aragonite is the stable solid phase. Watson[b] states that above 30° C. aragonite is the stable form of calcium carbonate in the presence of solutions of sodium chloride or ammonium chloride. Below that temperature, calcite is stable.

The experiments of Foote[c] have shown that at ordinary temperatures calcite is the stable form of calcium carbonate in solutions of carbon dioxide and also in mixed solutions of potassium carbonate and oxalate. The solubility of calcite is shown by electrical conductivity to be less than that of aragonite in carbon dioxide solutions. The conductivity of solutions saturated with carbon dioxide and calcium carbonate, either as calcite or aragonite, was measured at different temperatures. The following table gives the ratio of the conductivities.

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[a] For a review of the literature see Vater, Zeit. Kryst., **21**, 433 (1893).

[b] Chem. News, **63**, 109 (1891).

[c] Zeit. phys. Chem., **33**, 740 (1900).

TABLE LX.—*Ratio of conductivity of solutions of calcite and aragonite in water saturated with carbon dioxide.*

Temperature.	Aragonite / Calcite.
°C.	
8	1.147
25	1.130
41	1.124
48	1.115

It is apparent that the solubility of aragonite is higher than that of calcite, and therefore that calcite is the stable solid phase under these conditions. The ratio is smaller at higher temperatures, indicating that the solubility curves are approaching one another, and that at some higher temperature aragonite would probably become the stable phase. The effect of various salts has not been closely investigated.

A large amount of chemical work and of speculation has been done upon the conditions of the formation of dolomite in nature. The theory that dolomite resulted from the action of vapors of volcanic origin upon limestone rocks has long since been abandoned. All the authorities are now agreed that dolomite has been deposited from aqueous solution, either by deposition of the carbonates of calcium and magnesium together or by the action of water carrying magnesium salts on some form cf calcium carbonate. In nearly all the experiments upon the artificial formation of dolomite high temperature has been necessary. By heating a solution of magnesium sulphate with calcium carbonate in a sealed tube to 200° C. von Morlot[a] has obtained dolomite; Favre[b] used a solution of magnesium chloride; Hoppe-Seyler[c] used a solution of magnesium sulphate and calcium carbonate saturated with carbon dioxide above 100° C., and also confirmed the results of von Morlot and of Favre. Hunt[d] mixed equivalent quantities of the chlorides of magnesium and calcium and added sodium carbonate to the solution. At high temperature dolomite was formed. In all the above work calcium carbonate in the form of calcite was employed. Klement[e] has investigated the action of magnesium solutions upon aragonite under various conditions. He finds that at about 60° C. magnesium sulphate in saturated sodium chloride solutions begins to react upon aragonite to form dolomite, while under like conditions there is no reaction upon calcite. The extent of reaction increases with the time of contact, with the temperature, and with the concentration of salt in solution. There seems to be a maximum amount of magnesium carbonate in the solid for each temperature. At 91° C. 42 per cent of the solid is magnesium carbonate. The addition of the sodium chloride is equivalent to raising the temperature. In some further experiments coral was employed and was shown to act very similarly to aragonite. The final conclusion is that dolomite is formed by the action of sea water on aragonite, hot and in concentrated solution. Pfaff[a] has shown that dolomite separates from solution saturated with common salt, the carbonates of lime and magnesium, and carbon dioxide, in the presence of sulphides. The sulphides are derived in nature by the action of organic materials upon sulphates.

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[a] Haidinger's Naturwiss. Abhandl., **1**, 305 (1847).

[b] Arch. Sci. Phys. et Nat., **10**, 177 (1849).

[c] Zeit. deutsch. geol. Gesell., **27**, 495 (1875).

[d] Am. Jour. Sci. (2), **28**, 170, 365 (1859); **42**, 49 (1866).

[e] Bul. Soc. Belge. Geol., **8**, 219 (1894); Tschermaks Mitt., **14**, 526 (1895).

HYDRATES OF CALCIUM CARBONATE.

Rammelsberg[b] found in a river rhomboidal crystals of $CaCO_3.5H_2O$, which at 15° C. were dehydrated even under water. Pelouze[c] has obtained the same compound by exposing a solution of lime in sugar at a temperature of 7° to 8° C. After some weeks the above compound was formed. At a lower temperature $CaCO_3.6H_2O$ was produced when carbon dioxide was passed into the solution. This same precipitate was obtained by passing carbon dioxide into lime water at 0°, the precipitate being at first flocculent but soon changing to a heavy crystalline powder. The crystals change at 30° C. to a semifluid paste, which is a mixture of anhydrous calcium carbonate and water, a result which was confirmed by Hunt.[d] At 20° C. the same change occurs, but not so rapidly, and at lower temperatures the salt effloresces. At 0° the precipitate formed by mixing solutions of calcium chloride and sodium carbonate becomes crystalline on standing. Tschiwinsky[e] considers that the existence of the hydrate $CaCo_53H_2O$ has also been established and proposes the name *trihydrocalcite.*

SOLUBILITY OF CALCIUM CARBONATE IN WATER.

The results obtained by various experimenters on the solubility of calcium carbonate in water are far from concordant. In all likelihood this may be ascribed to impurities in the calcium carbonate—as, for instance, free lime would tend to increase the apparent solubility, if the calcium in solution was determined. Another reason is probably the presence of carbon dioxide in the water used by the early experimenters. Whipple and Mayer have more recently pointed out a very important source of error which has been almost disregarded by previous workers. The solubility of the glass vessels in water is sometimes much greater than that of the calcium carbonate, and these authors have tested this point by using glass of various kinds, and have found that Bohemian glass gave alkaline solutions which would have caused errors in solubility determinations of over 100 per cent. Jena glass they have found to be much more resistant to the action of water and have used this in their determinations, in which corrections have been made for the solubility of the glass vessels.

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[a] N. Jahresb. f. Min., Beilage Bd. **9,** 485 (1894).

[b] Ber. deutsch. chem. Ges., **4,** 469 (1871).

[c] Jour. Pharm. (4), **1,** 278 (1865).

[d] Am. Jour. Sci. (2), **42,** 49 (1866).

[e] Annuaire géol. et minéral. Russie, **8,** 245 (1906).

TABLE LXI.—*Solubility of calcium carbonate in water according to various experimenters.*

$CaCO_3$ per liter.	Temperature.	Observer.
Milligrams.	°C.	
63	....	Brandes.[a]
42-63	....	Buchholz.[a]
113	(Hot)	Fresenius.[b]
94	(Cold)	Fresenius.
20	....	Péligot.[c]
78	15	Kremers.[d]
16	....	Bineau.[e]
34	....	Hofmann.[f]
36	....	Weltzien.[g]
34	....	Chevalet.[h]
13.1	16	Schloesing.[i]
28.5	....	Anderson.[j]
27	....	Lubavin.[k]
10	8.7	Hollemann.[l]
12.5	23.7	Hollemann.
103	12	Pollacci.[m]
145	100	Pollacci.
12.8	18	Le Blanc and Novotný.[n]
20.7	95 to 100	Le Blanc and Novotný.
13	20	Whipple and Mayer.[o]

[a] See Comey, Dictionary of Chemical Solubilities (1896), 82.
[b] Ann. Chem. Pharm., **59**, 177 (1846).
[c] Jour. Pharm. (3), **19**, 324 (1851).
[d] Ann. Phys. Chem., **85**, 246 (1852).
[e] Ann. Chim. Phys. (3), **51**, 290 (1857).
[f] Jour. Chem. Soc., **4**, 381 (1852).
[g] Ann. Chem., **136**, 165 (1865).
[h] Bul. mens. de la soc. chim. de Paris. Aug. 1868, p. 90: abstr. in Zeit. anal. Chem., **8**, 91 (1869).
[i] Compt. rend., **74**, 1552 (1872).
[j] Proc. Roy. Soc. Edinburgh, **16**, 319 (1889).
[k] Jour. Russ. Chem. Soc., **24**, 389 (1892); abstr. in Jour. Chem. Soc., **64 II**, 373 (1893).
[l] Zeit. phys. Chem., **12**, 125 (1893).
[m] L'Orosi, **19**, 217 (1896); abstr. in Jour. Chem. Soc., **72 II**, 260 (1897).
[n] Zeit. anorg. Chem., **51**, 181 (1906).
[o] Jour. Infectious Diseases, Suppl. No. 2. 151 (1906).

SOLUBILITY OF CALCIUM CARBONATE IN AQUEOUS SOLUTIONS.

Carbon dioxide.

It was shown by Vogel[a] as early as 1814 that when carbon dioxide is passed into lime water all the lime dissolves and when the solution is heated calcium carbonate precipitates. Upon the addition of carbon dioxide to the solution again the precipitate redissolves. The experiments by Irving[b] indicate that heat is evolved both when the carbonate is being precipitated from lime water and also when the excess of carbon dioxide is redissolving the precipitate. The solubility of calcium carbonate in carbon dioxide solutions has been determined by many investigators and the early results are not at all concordant. The following table contains the results obtained by the various observers:

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[a] Bul. Pharm., **6**, 258 (1814).

[b] Chem. News, **63**, 192 (1891).

TABLE LXII.—*Solubility of calcium carbonate in water carrying carbon dioxide.*

$CaCO_3$ per liter.	Temperature.	Observer.
Grams.	°C.	
0.7003	0	Lassaigne.[a]
.8803	10	Lassaigne.
.6700		Bergmann.[b]
1.800 (burnt lime)		Bischof.[c]
2.800 (pure lime)		Bischof.
2.500		Marchand.[b]
1.0 to 1.5		Struve.[b]
3.0		Caro.[b]
1.165 to 2.305		Boutron and Boudet.[d]
0.9842	12	Warington.[e]
1.13 to 1.17	15	Treadwell and Reuter.[f]
1.30 to 1.31	13.2	Treadwell and Reuter.
1.43	28	Treadwell and Reuter.

[a] Jour. Chim. Méd. (3), **4**, 312 (1848).
[b] See Caro, Inaug.-Diss., Jena (1873); Arch. Pharm. (3), **4**, 145 (1874).
[c] See Treadwell and Reuter, Zeit. anorg. Chem., **17**, 170 (1898).
[d] Jour. Pharm. (3), **26**, 16 (1854).
[e] Jour. Chem. Soc., **19**, 296 (1866).
[f] Zeit. anorg. Chem., **17**, 170 (1898).

The above results show that the solubility depends very largely upon the purity of the original material. The solubility of calcium carbonate in water containing carbon dioxide is quite similar in kind to the solubility of dicalcium phosphate in phosphoric acid. Just as the amount of dicalcium phosphate in phosphoric acid solutions increases with increasing concentrations of acid,[a] so the amount of calcium carbonate in carbon dioxide solutions increases with increasing amounts of carbon dioxide. The difference between the two cases is that in one instance the solid phase changes above certain concentrations of the acid in solution while in the case of the carbonate no carbonate other than $CaCO_3$ has been recorded. The results of Schloesing[b] on the solubility of calcium carbonate in carbonic acid solutions at 16° C. are as follows:

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[a] See Bul. No. 41, Bureau of Soils, U. S. Dept. Agr. (1907).
[b] Compt. rend., **74**, 1552 (1872).

TABLE LXIII.—*Solubility of calcium carbonate in water containing carbon dioxide at various partial pressures at 16° C.*

Pressure CO_2.	CO_2 per liter.	$CaCO_3$ per liter.
Atmosphere.	*Milligrams.*	*Milligrams.*
0.000504	60.96	74.6
.000808	72.11	85.0
.0033	123.0	137.2
.01387	218.36	223.1
.0282	310.4	296.5
.05008	408.5	360.0
.1422	....	533.0
.2538	1,072.2	663.4
.4167	1,500.5	787.5
.5533	1,846.3	885.5
.7297	2,269.3	972.0
.9841	2,864.2	1,086.0

In a later paper[a] Schloesing has shown that the equation $p^m = ky$ describes the results. In the equation p is the pressure of CO_2, y is the amount of bicarbonate in solution, i. e., the amount of CaO calculated as $CaH_2(CO_3)_2$, and m and k are constants.

The empyrical formula of Schloesing has been modified by van't Hoff[b] to the form $C_1^{2.56} = KC_2$, where C_1 is the concentration of calcium bicarbonate and C_2 is the concentration of carbon dioxide, which in turn is proportional to the partial pressure of the gas. The coefficient 2.56 is known as the "activity coefficient," and is shown to vary with the dilution and at very extreme dilution equals 3. Bodländer[c] has calculated the dissociation constants at different dilutions and has recalculated Schloesing's results by a new formula, which describes the facts quite satisfactorily.

Where p is the pressure in atmospheres and y is the quantity of calcium bicarbonate in grams, the values of the constants are $m = 0.3787$ and $k = 0.9213$. Engel[d] has determined the solubility of calcium carbonate at pressures greater than 1 atmosphere and has found that the formula proposed by Schloesing describes the conditions up to 6 atmospheres, which was the highest pressure at which he worked.

TABLE LXIV.—*Solubility of calcium carbonate in water containing carbon dioxide at higher pressures.*

Pressure CO_2.	$CaCO_3$ per liter, observed.	$CaCO_3$ per liter, calculated.
Atmospheres.	*Milligrams.*	*Milligrams.*
1	1,079	1,085
2	1,403	1,411
4	1,820	1,834
6	2,109	2,139

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[a] Compt. rend., **75**, 70 (1872).

[b] Vorlesungen über theoretische und physikalische Chemie, I, 149.

[c] Zeit. phys. Chem., **35**, 23 (1900).

[d] Compt. rend., **101**, 949 (1885); Ann. Chim. Phys. (6), **13**, 344 (1888).

Treadwell and Reuter[a] have also determined the solubility of calcium carbonate in solutions of carbon dioxide at temperatures 10° to 14° C. (average 12°), with the following results:

TABLE LXV.—*Solubility of calcium carbonate in various solutions of carbon dioxide in water.*

Pressure of CO_2.	CO_2 per 100 c. c.	$CaH_2(CO_3)_2$ per 100 c. c.
Milligrams.	*Milligrams.*	*Milligrams.*
67.9	157.4	187.2
45.9	86.3	175.5
41.4	52.8	159.7
16.6	48.5	154.0
14.4	34.7	149.2
13.1	24.3	133.1
6.0	14.5	124.9
3.1	4.7	82.1
1.9	2.9	59.5
.6	....	40.2

The quantity of various samples of calcium carbonate which sea water would dissolve under various pressures has been determined by Reid.[b] In all the experiments the water contained about 1 gram of carbon dioxide per liter and the time of contact of the water and carbonate was 30 to 60 minutes.

TABLE LXVI.—*Solubility of calcium carbonate in water containing carbon dioxide.*

Material.	CO_2 per liter sea water.	Pressure.	Temperature.	$CaCO_3$ per liter.
	Grams.	*Tons.*	*° C.*	*Gram.*
Globigerina ooze I	1.0071	4	12.0	0.0906
	1.0494	4	12.0	.1486
	1.0523	4	9.0	.1191
	1.0203	4	9.0	.1080
	1.0102	(1 atm.)	12.2	.0568
	1.0744	(1 atm.)	10.0	.0572
	1.0777	2	8.3	.0999
Globigerina ooze II	1.0275	4	8.6	.0761
	1.0688	4	8.8	.0997
	1.0001	(1 atm.)	15.0	.0236
	1.0039	(1 atm.)	13.2	.0270
Coral sand I	1.0664	4	8.8	.1398
	1.0115	4	8.8	.1011
	1.0405	(1 atm.)	11.6	.0429
	1.0069	(1 atm.)	10.5	.0418
	.9666	(1 atm.)	12.2	.0407
Coral sand II	1.0596	4	9.1	.1220
	1.0738	(1 atm.)	9.0	.0391
Pteropods	1.0779	4	8.3	.1098
Crystalline	1.0557	(1 atm.)	11.0	.0516
	1.0307	4	8.3	.0371
	.9865	4	9.0	.0132
	.9845	(1 atm.)	10.0	.0102
	1.0410	....	12.2	.0082
	1.0513	....	12.2	.0050
	1.0440	....	13.1	.0034
	1.0532	....	14.7	.0048
Ground crystals	1.0536	....	12.6	.0322

The author draws the conclusion that "the amount of carbonate of lime dissolved at a pressure of 4 tons per square inch is so much greater than the amount dissolved at the ordinary pressure that I think it justifies the conclusion that the effect of pressure is to increase the rate of solution . . . . It is to be noted that, although these results may indicate that the solution of carbonate of lime in carbonic-acid water is more rapid under high pressures, it by no means follows that the solubility is *greater* than at the ordinary pressure (*ceteris peribus*)."

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[a] Zeit. anorg. Chem., **17**, 170 (1898).

[b] Proc. Roy. Soc. Edinburgh, **15**, 151 (1888).

Sodium hydroxide and carbonate.

In the process of manufacture of caustic alkali from alkaline carbonate and lime the relative solubility of lime and of calcium carbonate in solutions of the alkalies and alkaline carbonates is an important factor in determining the equilibrium conditions. The caustification of sodium carbonate would be represented by the reaction,

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3.$$

This is a four-component system, water being the fourth component, and consequently when the temperature is fixed there may be five phases at some definite concentration. There may be four phases over a range of conditions, i. e., the system is univariant. Several experimenters have found the equilibrium conditions where there are the two solid phases—calcium hydroxide and calcium carbonate—liquid and vapor.

The presence of the reaction product, caustic soda, in solution depresses very greatly the solubility of calcium hydroxide, and consequently is one factor tending to bring the reaction to a standstill. Reference has already been made[a] to the results of d'Anselme on the solubility of lime in solutions of caustic soda.

As the solubility of calcium carbonate in sodium hydroxide solutions has been found to be less than in pure water, for dilute solutions of the alkali, this fact would tend to cause the reaction to go to the right, i. e., toward the formation of calcium carbonate and sodium hydroxide. The following results by Le Blanc and Novotný[b] give the solubility of calcium carbonate in these solutions:

TABLE LXVII.—*Solubility of calcium carbonate in solutions of sodium hydroxide.*

NaOH per liter.	$CaCO_3$ per liter.	
	80° C.	95° to 100° C.
Gram.	*Milligrams.*	*Milligrams.*
0.0	12.8	20.7
.004	8.7	9.6
.04	4.2	6.9
.4	4.3	5.7

[a] Page 27.

[b] Zeit. anorg. Chem., 51, 181 (1906).

The equilibrium conditions have been found experimentally by Lunge and Schmid,[a] by Bödlander and Lucas,[b] and by Le Blanc and Novotný,[c] all of whom have shown that the change from sodium carbonate to sodium hydroxide is much more complete in dilut solutions than in concentrated solutions. For instance, the last-named authors have determined the composition of the two sodiu compounds present in the solution after an excess of lime has been added to varying solutions of sodium carbonate. At 100° C., w normal solution was used, about 99 per cent of the sodium was p as sodium hydroxide, while when a 3-normal (3N) solution was 93.6 per cent was present as hydroxide.

A recently published paper by Wegscheider [d] contains an investi tion of the nature of the solids formed when calcium carbonat mixed with solutions of sodium carbonate. Above certain concentrations it was found that a double compound of sodium and calcium carbonate was formed, $CaCO_3.Na_2CO_3.5H_2O$ at 11° C., while at and above 40° C. the double compound was of the composition $CaCO_3.Na_2CO_3.2H_2O$. The following table gives the composition of the "constant" solutions at various temperatures, the concentration with regard to calcium carbonate being too small for determination:

TABLE LXVIII.—*The "constant" solutions at various temperatures in the system, Na_2CO_3, $CaCO_3$, H_2O.*

Temperture.	Solid phases.	Concentration of solution.
° *C.*		
11	$CaCO_3$; $CaCO_3.Na_2CO_3.5H_2O$	0.86 normal Na_2CO_3.
40	$CaCO_3$; $CaCO_3.Na_2CO_3.2H_2O$	2.14 normal Na_2CO_3.
60	.....do	3.77 normal Na_2CO_3.
80	.....do	4.34

The same author has also published results upon the equilibria obtaining when free caustic soda is present in the solution.

TABLE LXIX.—*Solid phases at different concentrations and temperatures in the system, Na_2CO_3, $NaOH$, $CaCO_3$, H_2O.*

Temperture.	Solid phases.	Concentration of solution.	
		Na_2CO_3.	$NaOH$.
° *C.*			
60	$CaCO_3$; $CaCO_3.Na_2CO_3.2H_2O$	1.8 normal	2.6 normal.
60	.....do	3.7 normal	1.3 normal.
80	.....do	1.9 normal	2.9 normal.
80	.....do	3.3 normal	2.0 normal.

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[a] Ber. deutsch. chem. Ges., **18**, 3286 (1885).

[b] Zeit. Elektrochem., **11**, 186 (1905); Zeit. angew. Chem., **18**, 1137 (1905).

[c] Loc. cit.

[d] Ann. Chem., **351**, 87 (1907).

Sodium chloride.

Lubavin[a] has recorded the following qualitative result: 100 parts of a solution of sodium chloride (2.535 per cent) dissolves 0.0037 part of CaCO$_3$, calculated as CaO, or 0.0053 part calc-spar.

In the following experiments Cantoni and Goguelia[b] have determined the quantity of calcium carbonate in solutions of sodium chloride after the solution had stood in contact with solid calcium carbonate for 98 days at room temperature (12° to 18° C.).

TABLE LXX.—*Solubility of calcium carbonate in sodium chloride.*

[Time of contact, 98 days, at 12 to 18° C.]

NaCl in solution.	CaCO$_3$ per liter.
Per cent.	*Gram.*
5.85	0.0497
10.00	.0563
20.00	.0713

In the following experiments by Cameron, Bell, and Robinson[c] carbon dioxide was carefully excluded by using distilled water which had been boiled for some time before the solutions were made. This was necessary, for carbon dioxide, even at a partial vapor pressure equal to that in the ordinary air, is capable of producing a great increase in the solubility in sodium chloride solutions.

TABLE LXXI.—*Solubility of calcium carbonate in sodium chloride solutions free from carbon dioxide at 25°.*

Density $\frac{25°}{25°}$	NaCl in 100 grams H$_2$O.	CaCO$_3$ in 100 grams H$_2$O.
	Grams.	*Gram.*
1.0079	1.601	0.0079
1.0314	5.177	.0086
1.0466	9.25	.0094
1.0734	11.48	.0104
1.0944	16.66	.0106
1.1346	22.04	.0115
1.1794	30.50	.0119

Sodium chloride and carbon dioxide.

In the following tables are given the results of Treadwell and Reuter,[d] upon the solubility of calcium carbonate in water containing 5 grams of sodium chloride per liter and containing various quantities of carbon dioxide.

[a] Jour. Russ. Phys. Chem. Soc., **24**, 389 (1892); abstr. in Jour. Chem. Soc., **64 ii**, 373 (1893).

[b] Bul. Soc. Chem. (3), **33**, 13 (1905).

[c] Jour. Phys. Chem., **11**, 396 (1907).

[d] Zeit. anorg. Chem., **17**, 170 (1898).

TABLE LXXII.—*Solubility of calcium carbonate in various solutions of carbon dioxide in sodium chloride solution (½ per cent).*

Pressure of CO_2.	CO_2 per 100 c. c.	$CaH_2(CO_3)_2$ per 100 c. c.
Millimeters.	*Milligrams.*	*Milligrams.*
128.8	132.5	218.4
78.2	110.1	149.2
46.1	23.5	149.2
24.0	12.5	118.3
3.8	8.7	73.9
3.4	.3	49.0

By comparison with Table LXV it is apparent that the quantity both of free carbon dioxide and of calcium bicarbonate is less in salt solution than in pure water.

The following results are quoted from the work of Cameron and Seidell [a] upon the solubility of calcium carbonate in solutions of sodium chloride, the partial pressure of carbon dioxide in the vapor phase being that of ordinary air.

TABLE LXXIII.—*Solubility of calcium carbonate in aqueous solutions of sodium chloride at 25° C. in equilibrium with atmospheric air.*

NaCl per liter.	Calcium in solution, calculated as CaH_2CO_3 per liter.
Grams.	*Gram.*
0.0	0.1046
9.72	.1770
21.01	.2051
30.30	.2152
50.62	.2252
69.37	.2212
98.4	.2172
147.4	.1971
234.5	.1569
262.3	.1227

Table LXXIV gives the results where the pressure of the vapor phase, which consisted entirely of carbon dioxide and water vapor, was one atmosphere. This was attained by saturating the solutions with carbon dioxide at a lower temperature than 25° C. and removing the stopper of the bottles at intervals to allow the excess of the gas to escape after the bottles had been brought to the temperature of the experiment.

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[a] Bul. No. 18, Division of Soils, U. S. Dept. Agr. (1901), p. 58; Jour. Phys. Chem., **6**, 50 (1902).

TABLE LXXIV.—*Solubility of calcium carbonate in sodium chloride solutions saturated with carbon dioxide at 25° C. and one atmosphere pressure.*

Density $\frac{25^\circ}{25^\circ}$	NaCl in 100 grams H_2O.	$CaCO_3$ in 100 grams H_2O.
	Grams.	*Gram.*
1.0129	1.45	0.150
1.0499	5.69	.160
1.0501	6.48	.173
1.0759	11.06	.174
1.1015	15.83	.172
1.1246	19.62	.159
1.1789	29.89	.123
1.1957	35.85	.103

Sodium sulphate.

The following experiments were similar to those in Table LXXI, except that sodium sulphate was used instead of sodium chloride.

TABLE LXXV.—*Solubility of calcium carbonate in sodium sulphate solutions free from carbon dioxide at 25° C.*

Density $\frac{25^\circ}{25^\circ}$	Na_2SO_4 in 100 grams water.	$CaCO_3$ in 100 grams H_2O.
	Grams.	*Gram.*
1.0081	0.97	0.0151
1.0161	1.65	.0180
1.0363	4.90	.0262
1.1084	12.69	.0313
1.1200	14.55	.0322
1.1539	19.38	.0346
1.1615	21.02	.0343
1.1837	23.90	.0360

Sodium sulphate and carbon dioxide.

TABLE LXXVI.—*Solubility of calcium carbonate in aqueous solutions of sodium sulphate at 24° C. in equilibrium with atmospheric air.*

Na_2SO_4 per liter.	Total calcium calculated as $CaH_2(CO_3)_2$ per liter.	Calcium actually dissolved, as $CaH_2(CO_3)_2$ per liter.
Grams.	*Gram.*	*Gram.*
0.0	0.0925	0.0925
2.800	.1488	.1488
3.235	.1729	.1729
11.73	.233	.221
36.86	.324	.302
74.01	.396	.344
116.2	.458	.366
184.2	.563	.394
213.7	.591	.406
255.9	.665	.430

In the last table the results show that the solutions contained not only the bicarbonate but the normal carbonate of calcium as well, and that with increasing quantities of sodium sulphate the quantity of calcium carbonate increased also.

Sodium chloride in the presence of gypsum as solid phase.

It will be observed by comparison of Tables LXXIII and LXXVII that the presence of calcium sulphate in solution depresses the solubility of calcium carbonate, as might be expected in the case of a salt in solution with a common ion. In both these tables the solubility of calcium carbonate passes through a maximum.

In the following table are given the results of experiments by Cameron and Seidell[a] upon the solubility of gypsum and calcium carbonate in sodium chloride solutions, both gypsum and the carbonate being present as solid phases, and the solution being in equilibrium with the atmospheric air.

TABLE LXXVII.—*Solubility of calcium carbonate in aqueous solutions of sodium chloride, in contact with solid gypsum, in equilibrium with atmospheric air.*

$CaSO_4$ per liter.	$CaH_2(CO_3)_2$ per liter.	NaCl per liter.
Grams.	*Gram.*	*Grams.*
1.9298	0.0603	0.0
2.720	.0724	3.628
3.446	.0885	11.49
5.156	.1006	39.82
6.424	.0603	79.52
5.272	.0563	121.9
4.786	.0482	193.8
4.462	.0402	267.6

Sodium chloride and sulphate.

An excess of solid calcium carbonate was added to solutions containing varying quantities of sodium chloride and sodium sulphate, and after three months at 25° C., with frequent shaking, the solutions were analyzed. Table LXXVIII gives the data obtained in this work.

TABLE LXXVIII.—*Solubility of calcium carbonate in mixed solutions of sodium chloride and sodium sulphate at 25° C.*

Density $\frac{25°}{25°}$	NaCl in—		Na_2SO_4 in—		$CaCO_3$ in 100 grams H_2O.
	100 c. c.	100 grams H_2O.	100 c. c.	100 grams H_2O.	
	Grams.	*Grams.*	*Grams.*	*Grams.*	*Gram.*
1.2185	0.00	0.00	26.90	28.48	0.0239
1.2113	1.96	2.08	24.83	26.47	.0192
1.2115	6.43	6.93	21.67	23.36	.0137
1.2380	10.00	10.78	19.82	21.37	.0134
1.2378	10.07	10.89	19.39	20.98	.0137
1.2427	14.62	16.07	18.24	20.07	.0119
1.2570	17.16	19.18	18.43	20.74	.0116
1.2435	23.90	26.66	11.30	12.58	.0044
1.2442	27.30	31.15	8.79	10.00	.0046
1.2434	27.43	31.52	8.88	10.20	.0041
1.2270	28.32	32.17	6.74	7.65	.0043
1.2122	30.38	34.87	2.08	2.35	.0037
1.2020	31.52	35.70	0.00	0.00	.0036

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[a] Bul. No. 18, Division of Soils, U. S. Dept. Agr. (1901), p. 53.

These figures are in accord with the results of Cameron and Seidell, showing that calcium carbonate is more soluble in a saturated sodium sulphate solution than in one saturated with sodium chloride. It will be observed that as the concentration of sodium chloride in solution increases, the quantity of calcium carbonate decreases. The concentrations with respect to sodium chloride and sulphate are platted in figure 4. It has been found also that the presence of calcium carbonate in these small amounts has not appreciably affected the solubility of the more soluble chloride and sulphate of sodium.

In all these solutions calcium carbonate was the solid phase, and not a double compound. If a double compound of two calcium salts had been formed there would have been sodium carbonate in solution which would have caused the solutions to show a decided alkaline reaction. As the solutions were but very faintly, if at all, alkaline, no such change could have taken place. Further, f a double carbonate had resulted, the solution would have been ich in calcium salts and as the solution carried very little lime, it is apparent that such a change did not occur.

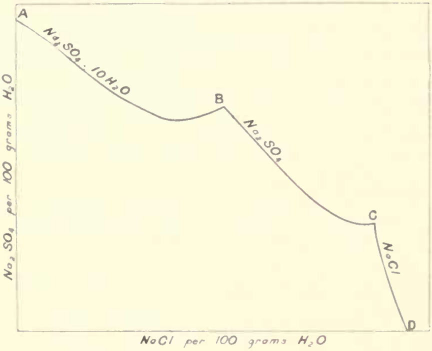

FIG. 4.—Solubility curves in the system—sodium sulphate, sodium chloride, and water at 25° C.

Owing to the very slight solubility of calcium carbonate in solutions of sodium chloride and sodium sulphate, it was expected that the presence of a salt ($CaSO_4$) with a common ion would depress this solubility even more. By the same procedure as was described in the preceding paragraph it was demonstrated that calcium carbonate underwent no change in these solutions.

TABLE LXXIX.—*Solubility of calcium sulphate and calcium carbonate in mixed solutions of sodium chloride and sodium sulphate at 25° C.*

Density $\frac{25°}{25°}$	NaCl in—		Na_2SO_4 in—		100g H_2O contains	
	100 c. c.	100 grams H_2O.	100 c. c.	100 grams H_2O.	$CaSO_4$	$CaCO_3$
	Grams.	*Grams.*	*Grams.*	*Grams.*	*Gram.*	*Gram.*
1.2109	2.76	2.94	23.78	25.35	0.2290	0.0163
1.2113	5.52	5.93	21.97	23.39	.1992	.0155
1.2442	28.12	32.18	8.52	9.50	.0301	.0065

Sodium chloride and sodium sulphate with carbon dioxide.

The variance of the system—sodium sulphate, sodium chloride, calcium sulphate, calcium carbonate, and water saturated with carbon dioxide—is not increased over that of the preceding system by the addition of the new component carbon dioxide, if at the same time the further condition is imposed, that the pressure of the vapor phase equals atmospheric pressure. In this case a field will represent solutions in contact with two solid phases; a boundary line, solutions in contact with three solid phases. "Constant" solutions will be in equilibrium with four solid phases.

For the experimental work on this system solutions saturated with either sodium sulphate or sodium chloride were put in contact with an excess of calcium carbonate, and the several solutions were saturated with carbon dioxide by passing the gas under pressure into the solutions at a low temperature. The bottles were then shaken at constant temperature, 25° C., and frequently unstoppered so that the pressure of the vapor phase was finally the atmospheric pressure. In all cases solid calcium sulphate, either as gypsum or a double sulphate, was found. Table LXXX gives the analytical data obtained for this system:

Table LXXX.—*Solubility of mixtures of calcium sulphate and calcium carbonate in mixed solutions of sodium chloride and sodium sulphate saturated with carbon dioxide at atmospheric pressure, at 25° C.*

Density $\frac{25^\circ}{25^\circ}$	NaCl in—		Na_2SO_4 in—		Calcium as calcium oxide in 100 grams H_2O.
	100 c. c.	100 grams H_2O.	100 c. c.	100 grams H_2O.	
	Grams.	*Grams.*	*Grams.*	*Grams.*	*Gram.*
1.2158	0.00	0.00	25.86	27.12	0.1430
1.2142	2.02	2.13	24.23	25.52	.1212
1.2109	4.00	4.28	22.81	24.22	.1148
1.2143	6.00	7.03	21.61	23.10	.1069
1.2248	9.98	10.77	19.53	21.09	.0812
1.2224	9.95	10.75	19.73	21.32	.0826
1.2281	11.31	12.31	19.15	20.84	.0726
1.2388	13.78	15.50	18.72	20.59	.0673
1.2590	18.67	20.40	19.80	21.61	....
1.2554	18.80	21.04	16.81	18.81	.0358
1.2332	21.46	23.81	11.61	12.88	....
1.2474	27.78	31.70	8.70	9.92	.0183
1.2429	28.47	32.73	5.56	6.26	.0291
1.2135	30.50	34.48	2.20	2.49	.0484
1.1957	31.14	35.46	0.00	0.00	.0490

In figure 5 the points A, B, C, D represent the "constant" solutions in the simple case where sodium sulphate and sodium chloride only are in solution. Upon the addition of calcium carbonate and calcium sulphate the points are displaced somewhat, the new positions being represented by A', B', C', D'. This figure has been distorted somewhat to magnify some of the differences which if drawn to scale would not be recognizable. The quantity of lime salts in solution at these points is also widely different and this has been indicated by the width of the strip $A\,B\,C\,D\,D'C'B'A'$, the points B and B' and the points C and C'', respectively, being close together. It has been found that over a certain range of concentrations, represented in the diagram by the field B' C'' F E, gypsum is not the stable salt of calcium but a double sulphate of calcium and sodium, $3Na_2SO_4.2CaSO_4$. Thus for every field there are two stable solid phases, one of which, calcium arbonate, exists over the whole figure. The other solid phases are sodium sulphate decahydrate, anhydrous sodium sulphate, sodium hloride, double sulphate, and gypsum for the fields marked 1, 2, 3, 4, nd 5, respectively.

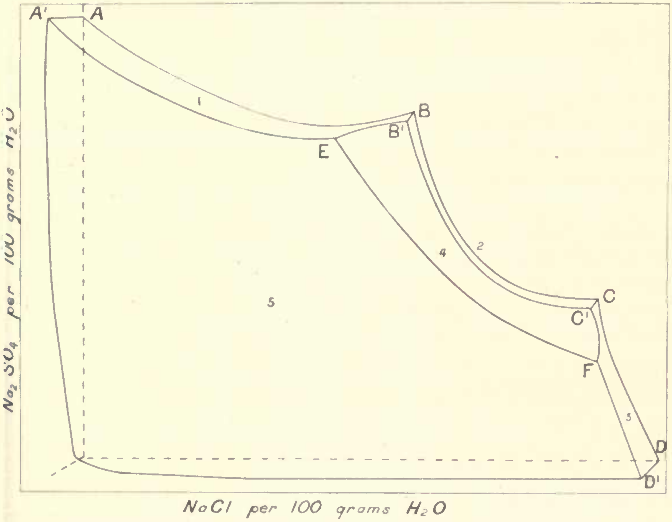

FIG. 5.—Diagram showing the solubility of calcium carbonate in solutions containing sodium chloride and sulphate, saturated with carbon dioxide at 25° C.

TABLE LXXXI.—*Data for constant solutions in the system—sodium chloride, sodium sulphate, calcium sulphate, calcium carbonate, carbon dioxide, and water at 25° C.*

Point.	Grams in 100 grams H_2O.			Solid phases.
	NaCl.	Na_2SO_4.	CaO.	
A....	0.00	27.12	0.1430	$Na_2SO_4.10H_2O$, $CaSO_4.2H_2O$, and $CaCO_3$.
E....	15.50	20.59	.0673	$Na_2SO_4.10H_2O$, $CaSO_4.2H_2O$, $CaCO_3$, and $2CaSO_4.3Na_2SO_4$.
B....	20.40	21.61	.0360	$Na_2SO_4.10H_2O$, $CaCO_3$, $2CaSO_4.3Na_2SO_4$, and Na_2SO_4.
C....	31.70	9.92	.0183	$CaCO_3$, NaCl, $2CaSO_4.3Na_2SO_4$, and Na_2SO_4.
F....	32.73	6.26	.0291	$CaCO_3$ NaCl, $2CaSO_4.3Na_2SO_4$, and $CaSO_4.2H_2O$.
D....	35.46	0.00	.0490	$CaCO_3$, NaCl, and $CaSO_4.2H_2O$.

Potassium chloride.

Cantoni and Goguelia[a] have determined the solubility of calcium carbonate in solutions of potassium chloride as follows:

TABLE LXXXII.—*Solubility of calcium carbonate in potassium chloride.*

[Time of contract, 98 days at 12°–18° C.]

KCl in solution.	$CaCO_3$ per liter.
Per cent.	*Gram.*
7.45	0.0748
10.0	.0742
20.0	.0828

It will be observed on comparison with Table LXX that potassium chloride has a greater solvent action on calcium carbonate than sodium chloride.

The following table contains results recently obtained in this laboratory:

TABLE LXXXIII.—*Solubility of calcium carbonate in aqueous solutions of potassium chloride at 25° C.*

Density $\frac{25°}{25°}$.	KCl in solution.	$CaCO_3$ in solution.
	Per cent.	*Per cent.*
1.000	0.00	0.0013
1.024	3.90	.0078
1.046	7.23	.0078
1.072	11.10	.0076
1.092	13.82	.0072
1.101	15.49	.0076
1.122	18.21	.0070
1.133	19.84	.0072
1.179	26.00	.0060

Potassium chloride and carbon dioxide.

The following table shows that the solubility of calcium carbonate in solutions of increasing content of potassium chloride passes through a maximum when the solutions are saturated with carbon dioxide:

TABLE LXXXIV.—*Solubility of calcium carbonate in aqueous solutions of potassium chloride saturated with carbon dioxide at atmospheric pressure at 25° C.*

KCl in solution.	$CaCO_3$ in solution.
Per cent.	*Per cent.*
3.90	0.145
7.23	.150
11.10	.166
13.82	.165
15.49	.167
18.21	.154
19.84	.140
26.00	.126

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[a] Bul. Soc. Chim. (3), **33**, 13 (1905).

Potassium sulphate.

The following table contains results obtained in this laboratory on the solubility of calcium carbonate in solutions of potassium sulphate at 25° C.:

ABLE LXXXV.—*Solubility of calcium carbonate in aqueous solutions of potassium sulphate at 25° C.*

Density $\frac{25°}{25°}$	K_2SO_4 in solution.	$CaCO_3$ in solution.
	Per cent.	*Per cent.*
1.010	1.60	0.0104
1.021	3.15	.0116
1.033	4.73	.0132
1.048	6.06	.0148
1.061	7.85	.0168
1.069	8.88	.0192
1.083	10.18	.0192
1.084	10.48	.0188

Potassium sulphate and carbon dioxide.

When calcium carbonate dissolves in water carrying carbonic acid and potassium sulphate there is formed in the metathetical reacion calcium sulphate. There is enough potassium sulphate and calcium sulphate in solution to exceed the solubility of syngenite ($K_2SO_4.CaSO_4.H_2O$) and consequently above a certain concentration of potassium sulphate, syngenite is the stable solid and not calcium carbonate, all of which passes into solution. The following table gives the percentages of sulphuric acid and lime in solution for various points on the calcium carbonate and syngenite curves:

TABLE LXXXVI.—*Solubility of calcium carbonate in aqueous solutions of potassium sulphate saturated with carbon dioxide at atmospheric pressure at 25° C.*

SO_3 in solution.	CaO in solution.
Per cent.	*Per cent.*
0.0	0.062
.69	.69
1.37	.69
1.67	.47
2.18	.30
2.99	.24

Sodium and potassium salts in general.

The precipitation of calcium carbonate in the cold is retarded or prevented by solutions of the alkali salts, chloride, sulphate, nitrate, carbonate, citrate, and phosphate,[a] if the solutions are not too concentrated. According to Dulong the alkali sulphates, phosphates, phosphites, and arsenates decompose calcium carbonate on boiling.

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[a] Storer, Am. Jour. Sci. (2), **35**, 41 (1858); Dulong, Ann. Chim., **82**, 273 (1812); Spiller, Jour. Chem. Soc., **10**, 110 (1858); Kippenberger, Zeit. anorg. Chem., **6**, 177 (1894).

Sea water.

In a paper upon the action of sea water upon lime carbonate Irvine and Young[a] have included results to show that the solubility of amorphous calcium carbonate in sea water was much greater than that of crystalline calcium carbonate. One part of amorphous calcium carbonate dissolves in 1,600 parts of sea water, while 8,000 parts of sea water are required to dissolve one part of crystalline calcium carbonate.

The following table contains the results of Anderson[b] upon the relative solubilities of various forms of calcium carbonate in distilled water, in sea water, and in water saturated with carbon dioxide at 10° to 15° C.

TABLE LXXXVII.—*Solubility of carbonate of lime in distilled water, in sea water, and in solution saturated with* CO_2.

	Distilled water.		Sea water.		Water saturated with CO_2.	
	$CaCO_3$ per liter.	Time.	$CaCO_3$ per liter.	Time.	$CaCO_3$ per liter.	Time.
	Gram.	*Hours.*	*Gram.*	*Hours.*	*Gram.*	*Hours.*
Calc-spar, massive	0.0147	120	0.0075	47		
Do.			.0046	120		
Do.			.0000	396	0.0815	24
Granular					.1285	24
Fine ground					.2036	24
Impalpable powder	.0251	46	.0082	47	.4720	24
Do.			.0052	120		
Do.			.0000	396		
Coral	.0285	96	.0237	96		
Amorphous $CaCO_3$	.2480		.6100			

The table shows that upon long standing in contact with the solvent the calcium carbonate in solution decreases, indicating the formation of a less soluble modification of calcium carbonate. It is also shown that the rate at which the solid is dissolved is increased by grinding the solid to a powder.

The solubility of calcium carbonate in an artificial sea water has been determined by Cohen and Raken[c] by agitating the mixture with a current of air. After 8 days at 15° C., 53.94 milligrams $CaCO_3$ were found in one liter, and after 17 days 57.27 milligrams $CaCO_3$ per liter.

Ammonium salts.

The presence of ammonium salts tends to hold calcium carbonate in solution, even in the case of the carbonate of ammonium which might be expected to cause complete precipitation of calcium carbonate. The solubility of calcium carbonate has been shown to be ncreased in the presence of the chloride, carbonate, sulphate, nitrate, acetate, and succinate of ammonium.[a] Bertrand has given the amounts of different ammonium salts which are required to hold in solution 1 gram of calcium carbonate, viz, 13.98 grams ammonium chloride, 8.38 grams ammonium sulphate, and 14.44 grams ammonium nitrate, but the absolute concentrations are not given. When the solution of calcium carbonate in ammonium chloride is heated to boiling there is decomposition with the formation of ammonia and carbon dioxide.[b] The same decomposition has been shown in the case of the other ammonium salts, sulphate, sulphite, phosphate, phosphite, and oxalate.[c] On cooling the solutions of calcium carbonate in ammonium salts, the solid carbonate crystallizes out.

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[a] Proc. Roy. Soc. Edinburgh, **15**, 316 (1888).

[b] Proc. Roy. Soc. Edinburgh, **16**, 319 (1889).

[c] Proc. K. Akad. Wetensch. Amsterdam, **3**, 63 (1900); abstr. in Jour. Chem. Soc., **72 ii**, 725 (1900).

Calcium and magnesium salts.

Calcium carbonate is soluble in dilute solutions of calcium and magnesium sulphates and chlorides.[d] According to Hunt a solution containing 3 or 4 grams of magnesium sulphate per liter will dissolve over 1 gram of calcium carbonate. It is also soluble in calcium sucrate.[e]

When calcium acetate solution is added to potassium carbonate solution, the precipitate is not calcium carbonate, but a double carbonate of calcium and potassium, $CaK_2(CO_3)_2$.[f]

The action of water carrying carbon dioxide and the chloride of lime or magnesia upon various lime algæ has been investigated by Vesterberg.[g] In the presence of sodium chloride relatively more magnesia is dissolved than in the presence of calcium chloride or in the presence of magnesium chloride.

Other compounds.

Compounds which give acid solutions, such as stannic chloride and the chloride or nitrate of iron, aluminum or chromium, dissolve calcium carbonate with the evolution of carbon dioxide. As the acidity is reduced the hydroxide or oxide is precipitated. Calcium carbonate is not acted upon by concentrated nitric acid,[h] for it becomes coated with calcium nitrate, which is insoluble in the concentrated acid. Upon the addition of water, however, a brisk action begins.

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[a] Wittstein, Repert. Pharm. (2), **7**, 18 (1836); Smith, Phil. Mag. (3), **9**, 542 (1836); Brett, Phil. Mag.(3), **10**, 95 (1837); Wackenroder, Ann. Chem. Pharm., **41**, 315 (1842); Fresenius, Ann. Chem. Pharm., **59**, 117 (1846); Storer, Am. Jour. Sci. (2), **25**, 41 (1858); Bertrand, Monit. Sci. (3), **10**, 477 (1880).

[b] Demarçay, Ann. Chim. (2), **55**, 398 (1834); Schrieb, Zeit. angew. Chem., **2**, 211 (1889); Cantoni and Goguelia, Bul. Soc. Chim. (3), **31**, 282 (1904); **33**, 13 (1905).

[c] Dulong, Ann. Chim., **82**, 273 (1812).

[d] Cousté, Compt. rend., **35**, 186 (1852); Hunt, Am. Jour. Sci. (2), **26**, 109 (1858).

[e] Barreswill, Jour. Pharm. (3), **19**, 330 (1851).

[f] Reynolds, Jour. Chem. Soc., **73**, 262 (1898).

[g] Bul. Geol. Inst. Upsala, **5**, 97 (1900); **6**, 254 (1903).

[h] Barreswill, Jour. Pharm. (3), **3**, 290 (1843).

The rate at which calcium carbonate in the form of Iceland spar is dissolved by acids has been shown by Spring[a] to be independent of the chemical nature of inorganic acids whose calcium salts are soluble. It was also proved that the velocity depended upon the surface exposed, and that at low temperatures the rate was proportional to the concentration of the acid.

In solutions of hydrochloric and nitric acids in absolute ethyl alcohol, calcium carbonate is readily attacked, but not by solutions of sulphuric acid.[b] The same results have been found for solutions of these acids in the other organic solvents, acetone and methyl alcohol.[c] The addition of water to the sulphuric acid mixture causes the reaction to be very much accelerated. Acetic acid acts similarly to sulphuric acid. In all these cases the occurrence of chemical reaction depends on the solubility or insolubility of the calcium salt of the acid in the solvent employed.

GENERAL CONCLUSIONS.

1. Calcite is the stable form of calcium carbonate at ordinary temperatures. In concentrated salt solutions or at the higher concentrations, aragonite is probably the stable phase.

2. Regarding the formation of natural dolomite, the literature affords no satisfactory explanation. High temperatures and concentrated solution seem to be necessary for its formation.

3. At the low temperatures calcium carbonate forms a hydrate with five molecules of water of crystallization.

4. The results upon the solubility of calcium carbonate in water are very discordant, but there is good authority for the generalization that it is more soluble in hot water than in cold.

5. The solubility of calcium carbonate in water containing carbon dioxide increases as the quantity of carbon dioxide in solution increases.

6. The solubility of calcium carbonate is depressed by the addition of caustic soda to the solution.

7. The caustification of sodium carbonate by lime is more complete in dilute solution.

8. Calcium carbonate forms with sodium carbonate two double compounds, whose stability depends on the temperature and the concentration of the solution with which they are in contact.

9. The solubility of calcium carbonate is increased by addition of sodium chloride or of sodium sulphate.

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[a] Bul. Acad. Roy. Belg. (3), **14**, 725 (1887); Bul. Soc. Chim. (3), **3**, 177 (1890).

[b] Carette, Thesis, Lille, 1900. See Vallée, Compt. rend., **132**, 677 (1901).

[c] Vallée, Loc. cit.

10. When the pressure of carbon dioxide is one atmosphere, the solubility of calcium carbonate passes through a maximum upon increasing the concentration of sodium chloride in solution, both in the presence and absence of gypsum. When increasing quantities of sodium sulphate are added, however, the solubility of the carbonate constantly increases.

11. The solubility of calcium carbonate at 25° C. is about six times as great in a saturated solution of sodium sulphate as in a saturated solution of sodium chloride.

12. When certain solutions containing sodium sulphate and chloride are saturated with carbon dioxide in the presence of calcium carbonate a new solid phase appears, $2CaSO_4.3Na_2SO_4$.

13. When the pressure of carbon dioxide is one atmosphere, the solubility of calcium carbonate passes through a maximum upon increasing the concentration of potassium chloride or sulphate in solution.

14. In the presence of sea water the crystalline modification of calcium carbonate is more stable than the amorphous form.

15. In general the presence of ammonium salts in solution increases the solubility of calcium carbonate. On heating, carbon dioxide and ammonia escape.

16. Calcium and magnesium salts have a solvent action upon calcium carbonate.

17. Salt solutions which have an acid reaction tend to dissolve calcium carbonate.

18. Calcium carbonate is soluble in strong acids, whose lime salts are soluble in the strong acid.

MAGNESIA.

SOLUBILITY OF MAGNESIA IN WATER.

The wide variations between the results of the various observers have been attributed by Whipple and Mayer to two causes—the solvent action of carbon dioxide dissolved from the air and the action of water upon the glass vessels in which the solutions were contained. Water reacts with many kinds of glass, dissolving the bases; and as some of the determinations were made by estimating the alkalinity of the solution, this quantity of alkali dissolved from the glass walls introduced very large errors. To these two causes of discrepancy might be added a third probable source of error. The presence of very minute quantities of impurities in the magnesia, such as lime, would introduce comparatively large errors into the determinations of the solubility of magnesia. The following table gives the results of the various observers.

TABLE LXXXVIII.—*Solubility of magnesium hydroxide in water.*

$Mg(OH)_2$ per liter.	Temperature.	Observer.
Milligrams.	°C.	
250	15	Fyfe.[a]
250	15	Henry.[b]
26	(Hot and cold.)	Fresenius.[c]
5-10	(Cold.)	Bineau.[d]
9	18	Kohlrausch and Rose.[e]
8	18	Dupré and Bialas.[f]
12	22	Whipple and Mayer.[g]

[a] Cited by Henry, Jour. Pharm., **13.** 1 (1827).
[b] Jour. Pharm., **13,** 1 (1827).
[c] Ann. Chem. Pharm., **59,** 117 (1847).
[d] Compt. rend., **41,** 510 (1855).
[e] Zeit. phys. Chem., **12,** 241 (1893).
[f] Zeit. angew. Chem., **16,** 54 (1903).
[g] Jour. Infectious Diseases, Suppl. No. 2, 151 (1906).

SOLUBILITY OF MAGNESIA IN AQUEOUS SOLUTIONS.

The solubility of magnesia is given by Precht [a] as 16 milligrams per liter in water containing potash. The presence of ammonium salts increases the solubility of magnesia, even in the presence of free ammonia.[b] When warm solutions of ammonium salts are decomposed by magnesia, ammonia is evolved. Sodium and potassium salts act similarly in their solvent action on magnesia but to a far lesser degree.[c] Maigret [d] has recently investigated the solubility of magnesia in a sodium chloride solution containing sodium hydroxide and shows that the presence of the free base reduces the solubility.

TABLE LXXXIX.—*Solubility of magnesia in solutions of sodium chloride containing sodium hydroxide.*

NaCl per liter.	MgO per liter.	
	With 0.8 gram NaOH per liter.	With 4.0 grams NaOH per liter.
Grams.	*Gram.*	*Gram.*
125	0.07	0.03
140	.045	.0
160	.0	.0

The solubility of magnesia is increased by glucose.[e] Bernard and Ehrmann [f] have, however, used the insolubility of magnesia in sugar solutions as a means of separating lime and magnesia. The following table of Herz and Muhs[a] gives the solubility of magnesium hydroxide in solutions containing ammonium salts:

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[a] Zeit. anal. Chem., **18,** 439 (1879).

[b] Warington, Jour. Chem. Soc., **18,** 27 (1865); Lovén, Zeit. anorg. Chem., **11,** 404 (1896); Treadwell, Zeit. anorg. Chem., **37,** 326 (1903); Herz and Muhs, Zeit. anorg. Chem., **38,** 138 (1904).

[c] Warington, Jour. Chem. Soc., **18,** 27 (1865).

[d] Bul. Soc. Chim. (3), **33,** 631 (1905).

[e] Fleury, Jour. Pharm. (4), **28,** 400 (1878).

[f] Compt. rend., **83,** 1239 (1876).

TABLE XC.—*Solubility of magnesia in ammonium salt solutions at 29° C.*

NH_4Cl per liter.	$Mg(OH)_2$ per liter.	NH_4NO_3 per liter.	$Mg(OH)_2$ per liter.
Grams.	*Grams.*	*Grams.*	*Grams.*
4.13	1.43	6.09	1.45
5.67	1.86	14.69	2.43
9.21	2.60	....	....
13.39	3.15	....	....
20.86	4.55	....	....

When recently ignited magnesia is added to a concentrated solution of magnesium chloride a very thick mass is formed which according to Sorel[b] is composed of an oxychloride of magnesium. Bender[c] has given it the formula $MgCl_2.5MgO.17H_2O$, Davis[d] the formula $MgCl_2.5MgO.13H_2O$, and Krause[e] the formula $MgCl_2.10MgO.14H_2O$ when dried at 110°, and $MgCl_2.10MgO.18H_2O$ when air dried. André[f] has found the heat of formation of the following oxychlorides, $MgCl_2.MgO.16H_2O$, $MgCl_2.MgO.6H_2O$, $MgCl_2.10MgO.13H_2O$, and $MgCl_2.10MgO.16H_2O$. The following crystalline basic bromides of magnesium have been prepared by Tassilly,[g] $MgBr_2.3MgO.12H_2O$, $MgBr_2.3MgO.6H_2O$.

GENERAL CONCLUSIONS.

1. The various determinations of the solubility of magnesia in water are not in accord. The modern writers, however, agree that this solubility is about 10 milligrams per liter at 20° C.

2. The solubility of magnesia is augmented by various salts, including magnesium salts, but is depressed by caustic alkalies.

3. Several basic chlorides and bromides of magnesium have been recorded in the literature, and are obtained by adding magnesia to a solution of the chloride or bromide of magnesium.

MAGNESIUM CARBONATE.

MODIFICATIONS AND HYDRATES OF MAGNESIUM CARBONATE.

The mineral magnesite is probably insoluble in water[h] and is not affected by boiling with water or aqueous solutions of alkaline carbonates. Artificial magnesium carbonate has been prepared by Engel[i] by heating to 130° C. the double carbonate of magnesium and ammonium. This anhydrous magnesium carbonate "slakes" in moist air, being easily converted into the hydrated form $MgCO_3.3H_2O$. On account of its behavior when heated Davis has given it the formula $(MgOH)(HCO_3).2H_2O$, 2 molecules of water being lost when the compound is heated to 95° or 100° C., at which temperature the substance becomes constant in weight as soon as the composition $MgCO_3.H_2O$ or $(MgOH)(HCO_3)$ is reached. At 125° C. the rate of change is very much more rapid. This same change can be brought about by heating the compound $(MgOH)(HCO_3).2H_2O$ with xylene, the water which is liberated being removed as fast as it is formed and consequently hydrolysis of the salt can not ensue.

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[a] Zeit. anorg. Chem., **38**, 140 (1904).

[b] Compt. rend., **65**, 102 (1867).

[c] Ann. Chem. Pharm., **159**, 341 (1871).

[d] Chem. News, **25**, 258 (1872).

[e] Ann. Chem. Pharm., **165**, 38 (1873).

[f] Compt. rend., **94**, 444 (1882).

[g] Compt. rend., **125**, 605 (1897); Bul. Soc. Chim. (3), **17**, 964 (1897).

[h] See Davis, Jour. Soc. Chem. Ind., **25**, 788 (1906).

[i] Compt. rend., **129**, 598 (1899).

By heating the above compound with water, however, a product is obtained of widely varying composition, depending upon the time and upon the temperature. The product has been considered as a basic carbonate of magnesium. Davis, however, by a microscopical examination has proved that it is in all cases a mixture of two solid phases and not a single compound. As the dehydration of the compound $(MgOH)(HCO_3).2H_2O$ requires considerable time and as the equilibrium between the compound $(MgOH)(HCO_3)$ and the hydroxide of magnesium is reached but slowly, the solid residue was found to consist of two and often three solid phases, indicating that equilibrium had not been attained. The two reactions may be written:

$$(MgOH)(HCO_3).2H_2O = (MgOH)(HCO_3) + 2H_2O,$$
$$(MgOH)(HCO_3) = Mg(OH)_2 + CO_2.$$

The solid phases consisted of the two hydrates of magnesium carbonate and of magnesium hydroxide.

When a magnesium salt is precipitated by means of a solution of an alkaline carbonate, a basic carbonate, or a double carbonate may first be formed, but experiments by Berzelius,[a] Fritsche,[b] Favre,[c] Jacquelain,[d] and Rose[e] have proved that upon standing for several days the precipitate becomes crystalline and corresponds to the formula $MgCO_3.3H_2O$. Kippenberger[f] has ascribed the formula $MgCO_3.\frac{15}{4}H_2O$ to this compound and Marignac[g] and Damour[h] have obtained $MgCO_3.4H_2O$.

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[a] Ann. Chim. Phys. (2), **14**, 363 (1820).
[b] Ann. Phys. Chem., **37**, 304 (1836).
[c] Ann. Chim. Phys. (3), **10**, 474 (1844).
[d] Ann. Chim. Phys. (3), **32**, 195 (1851).
[e] Ann. Phys. Chem., **84**, 461 (1851).
[f] Zeit. anorg. Chem., **6**, 177 (1894).
[g] Compt. rend., **42**, 288 (1856).
[h] Compt. rend., **44**, 561 (1857).

DOUBLE CARBONATES CONTAINING MAGNESIUM CARBONATE.

When carbon dioxide is passed into a suspension of magnesia to saturation the solution contains 10.7 grams of magnesia (MgO) in one liter and when an equal volume of 95 per cent alcohol is added a precipitate of magnesium carbonate forms, $MgCO_3.3H_2O$.[a]

By mixing solutions of a soluble magnesium salt with a solution of an alkaline carbonate various compounds have been obtained:[b] $K_2CO_3.MgCO_3.4H_2O$, $KHCO_3.MgCO_3.8H_2O$, $Na_2CO_3.MgCO_3$, and $Na_2CO_3MgCO_3.15H_2O$. Kippenberger[c] has shown that the precipitate obtained by mixing sodium carbonate and magnesium sulphate in equimolecular proportions is soluble in the alkaline bicarbonates. After several hours, however, the hydrated magnesium carbonate separates in large crystals and the quantity of magnesium carbonate in solution decreases after several days. Freshly precipitated magnesium carbonate is soluble in magnesium chloride and in magnesium sulphate solutions.

The double carbonates of sodium and magnesium undergo decomposition upon heating in water, sodium carbonate passing into solution and the solid residue consisting of a mixture of magnesium hydroxide and carbonate.[d] It is difficult, however, to remove the last traces of the alkali from the solid, even by boiling, and in order to obtain pure magnesium carbonate Davis has dissolved the solid residue in water saturated with carbon dioxide and then boiled off the carbon dioxide, leaving a residue free from traces of sodium salts.

SOLUBILITY OF MAGNESIUM CARBONATE IN AQUEOUS SOLUTIONS.

Carbon dioxide.

Owing to the slow transformation of one modification into another, the solubility of magnesium carbonate in water and in aqueous solutions depends upon the source of the solid employed and on the time of contact. Engel[e] has given the results of Beckurts and of Bineau, who undoubtedly worked with widely different samples and under different conditions. One liter of water saturated with carbon dioxide dissolves 1.31 grams magnesium carbonate according to Wagner and Merckel, 8.39 grams according to Beckurts, and 23.3 grams according to Bineau. The following table gives the results of Wagner and Merckel,[f] who found the effect of increasing the quantity of carbon dioxide in solution:

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[a] Monhaupt, Chem. Zeit., **28**, 868 (1904).

[b] See Graham-Otto, Lehrbuch anorg. Chem., 5th edn., III, 730-753.

[c] Zeit. anorg. Chem., **6**, 177 (1894).

[d] Davis, loc. cit.

[e] Ann. Chim. Phys. (6), **13**, 344 (1888).

[f] Jour. prakt. Chem., **102**, 233 (1867).

TABLE XCI.—*Solubility of magnesium carbonate in water saturated with carbon dioxide at 5° C.*

Pressure.	$MgCO_3$ per liter.
Atmospheres.	*Grams.*
1	1.31
2	1.34
3	7.46
4	9.03
5	9.09
6	13.15

Engel and Ville[a] have also found that by increasing the pressure of the carbon dioxide and by decreasing the temperature the quantity of magnesium carbonate in solution increased.

TABLE XCII.—*Solubility of magnesium carbonate in water saturated with carbon dioxide at various pressures (Engel and Ville).*

T=19.5° C.		T=12° C.	
Pressure.	$MgCO_3$ per liter.	Pressure.	$MgCO_3$ per liter.
Atmospheres.	*Grams.*	*Atmospheres.*	*Grams.*
1	25.79	0.5	20.5
2.1	33.11	1	26.5
3.2	37.30	1.5	31.0
4.7	43.50	2	34.0
5.6	46.20	2.5	36.4
6.2	48.50	3	39.0
7.5	51.20	4	42.8
9.0	56.59	6	50.6

TABLE XCIII.—*Solubility of magnesium carbonate in water saturated with carbon dioxide at various temperatures. Pressure = 1 atmosphere (Engel and Ville).*

Temperature.	$MgCO_3$ per liter.
° C.	*Grams.*
13.4	28.45
19.5	25.79
29.3	21.95
46.0	15.7
62.0	10.35
70.0	8.1
82.0	4.9
90.0	2.4
100.0	0.0

TABLE XCIV.—*Solubility of magnesium carbonate in water saturated with carbon dioxide at various temperatures. Pressure=1 atmosphere (Engel).*

Temperature.	$MgCO_3$ per liter.
° C.	*Grams.*
3.5	36.5
12.0	26.5
18.0	22.1
22.0	20.0
30.0	15.8
40.0	11.8
50.0	9.5

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[a] Compt. rend., **93,** 340 (1881); see also Engel, Compt. rend., **100,** 444 (1885); Ann. Chim. Phys. (6), **13,** 344 (1888).

Bodländer [a] has attempted to obtain a formula of the same form as that derived to express the solubility of calcium carbonate in water containing carbon dioxide, but has found it necessary to assume the presence of ions in solution of the form $(MgCO_3)_nMgOH$.

Finally, Treadwell and Reuter [b] have shown that at the lower concentrations there is less carbon dioxide in solution than corresponds to the formula $MgH_2(CO_3)_2$, a conclusion which has been confirmed by Rinne.[c] These results are shown in the following table:

TABLE XCV.—*Solubility of magnesium carbonate in water containing carbon dioxide at 12° to 15° C. (average, 14° C.).*

Partial pressure of CO_2.	CO_2 per 100 c.c. solution.	$MgH_2(CO_3)_2$ per 100 c.c. solution.	$MgCO_3$ per 100 c. c. solution.
Millimeters.	*Milligrams.*	*Milligrams.*	*Milligrams.*
143.3	119.0	1,210.5	....
41.6	86.6	1,210.5	....
33.8	3.5	1,210.5	....
11.7	....	1,076.6	77.3
10.3	....	762.9	76.5
8.2	....	595.2	80.7
4.7	....	366.3	70.1
4.6	....	341.7	75.8
2.5	....	263.2	74.8
1.6	....	222.9	77.1
1.1	....	216.9	71.0
0.3	....	203.6	71.1
....	....	203.3	68.5
....	....	196.0	70.2
....	....	203.6	62.5
....	....	195.4	61.6
....	....	195.4	64.1

Rinne [d] has boiled a solution of magnesium carbonate in water containing carbon dioxide for several hours, and found that the quantity of magnesia in solution constantly decreased.

Sodium chloride.

The solubility of magnesium carbonate in various aqueous solutions of sodium salts has been recorded by Cameron and Seidell.[e]

TABLE XCVI.—*Solubility of magnesium carbonate in solutions of sodium chloride free of carbon dioxide.*

Weight of liter solution.	NaCl per liter.	$MgCO_3$ per liter.
Grams.	*Grams.*	*Gram.*
996.92	0.0	0.176
1,016.82	28.0	.418
1,041.09	59.5	.527
1,070.50	106.3	.585
1,094.53	147.4	.544
1,142.48	231.1	.460
1,170.14	272.9	.393
1,199.28	331.4	.293

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[a] Zeit. phys. Chem., **35**, 23 (1900).

[b] Zeit. anorg. Chem., **17**, 170 (1898).

[c] Chem. Zeit., **31**, 125 (1907).

[d] Loc. cit.

[e] Jour. Phys. Chem., **7**, 578 (1903).

Sodium chloride and carbon dioxide.

TABLE XCVII.—*Solubility of magnesium carbonate in solutions of sodium chloride saturated with atmospheric air at 25° C.*

NaCl per liter.	$Mg(HCO_3)$ per liter.
Grams.	*Grams.*
7.0	30.64
56.5	30.18
119.7	27.88
163.9	24.96
224.8	20.78
306.6	10.75

Sodium sulphate.

TABLE XCVIII.—*Solubility of magnesium carbonate in solutions of sodium sulphate free of carbon dioxide.*

24° C.			35° C.		
Weight of liter solution.	Na_2SO_4 per liter.	$MgCO_3$ per liter.	Weight per liter solution.	Na_2SO_4 per liter.	$MgCO_3$ per liter.
Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*
997.52	0.0	0.216	995.15	0.32	0.131
1,021.24	25.12	.586	1,032.89	41.84	.577
1,047.60	54.76	.828	1,067.23	81.84	.753
1,080.95	95.68	1.020	1,094.77	116.56	.904
1,133.85	160.80	1.230	1,120.38	148.56	.962
1,157.34	191.90	1.280	1,151.70	186.7	1.047
1,206.03	254.60	1.338	1,179.82	224.0	1.088
1,223.91	278.50	1.338	1,196.32	247.2	1.110
1,241.99	305.10	1.388	1,236.52	299.2	1.130

GENERAL CONCLUSIONS.

1. Magnesium carbonate forms several hydrates, each of which is stable within limits of concentration and temperature.

2. Magnesium carbonate forms several double compounds with the alkali carbonates.

3. The solubility of magnesium carbonate is greatly increased by the addition of carbon dioxide to the solution, the solubility being less at the higher temperatures.

4. The solubility of magnesium carbonate passes through a maximum as the concentration of sodium chloride increases, but in the presence of carbon dioxide this solubility is depressed by addition of sodium chloride.

5. The solubility in solutions of sodium sulphate is increased by increasing the concentration of the latter.

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MOISTURE CONTENT AND PHYSICAL CONDITION OF SOILS.

BY

FRANK K. CAMERON AND FRANCIS E. GALLAGHER.

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MILTON WHITNEY, Chief.

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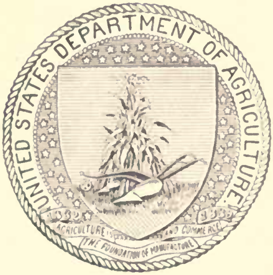

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BUREAU OF SOILS.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., September 13, 1907.

Sir: I have the honor to transmit herewith the manuscript of a echnical article entitled Moisture Content and Physical Condition n Soils. In accordance with your suggestion, it has been submitted o Assistant Secretary Hays, who concurs with me in recommending for publication.

Respectfully,

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

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MOISTURE CONTENT AND PHYSICAL CONDITION OF SOILS.

INTRODUCTION.

It is generally recognized that the physical properties of a soil determining crop adaptation and growth are moisture supply, aeration, temperature, texture and structure, and "physical condition." Under these heads fall practically all physical investigations on the soil. Of course "physical condition" is by far the most important in practice, because it is the one factor directly under the control of the agriculturist, such control of the others as may be possible being usually but incidental to control of the last. Everyone who has had any experience can judge with comparative readiness as to whether a soil is in good or poor physical condition. But apparently no two observers will agree entirely as to the basis of their judgments. It is said that a soil in good physical condition must be loose, friable, loamy, have a crumb structure, work well, have a "live" look, etc., properties which are sufficiently definite to be recognized readily, but which are not susceptible of exact measurement and quantitative expression. It is evident that a comparison of soils as to their physical condition is mainly a matter of individual judgment, subject to the limitations and errors of a personal equation; and while physical condition is the most readily under practical control, paradoxical as it may seem, it is the most difficult of soil properties to study. This is because the concept or idea of "physical condition" is a summation of a number of properties rather than any one property, and because no satisfactory method of measuring this sum has yet been devised. Nevertheless, much can be done to advance our knowledge of this important subject by studies in the field and, especially, in the laboratory.

In the present bulletin are given the results of an investigation on the relation of physical condition to moisture content, in which the soils were put into different states with different amounts of water present and then subjected to various physical tests yielding measurable results. In this work the judgment of several experienced greenhouse men was available for determining the physical condition of the samples before and after the several measurements were made. It has been found that the physical condition of the soil is connected in the most intimate way with its water content. Not only is this true of its general behavior and appearance, its "workability," etc., but systematic quantitative measurements on penetrability, volume changes, apparent specific gravity, and rate of evaporation showed a direct dependence on the water content. All these properties varied regularly with regular change in the water content when the sample was in the best possible physical condition obtainable with any given water content.

One particular water content has been given special consideration. It is perfectly well known to agriculturists generally and greenhouse men especially that there is a particular water content (or perhaps a more or less narrow range of water content) differing with each soil at which plants grow best, other conditions being the same. This is popularly known as the "optimum" water content, and is supposed to be that content from which plants draw most readily their needed supply; in other words, the optimum water content is supposed to be determined by the physiological necessities of the plant rather than by the physical properties of the soil. There are difficulties, however, for which this view fails to offer sufficient and satisfactory explanation. Plants can do quite well in soils containing considerably less than the optimum water content, other conditions being favorable. That is to say, there is no decided or sharp falling off in the plant growth corresponding with a lowering of the water content until the drought limit is approached, a limit generally much below the "optimum;" and, on the other hand, there is no especial difficulty in carrying some of our common crops to a satisfactory maturity in water cultures. The investigation described in the following pages shows conclusively not only that physical condition and the several properties on which it depends have an intimate relation with the water content of the soil, but that there is marked accentuation in these properties at a critical water content; and that this critical content is identical with the optimum water content. The *moisture-penetration* curve shows a minimum force required for penetration at the optimum water content; the *moisture-apparent specific gravity* curve shows a minimum point at the optimum water content; the curves for *evaporation* show a marked difference in the rate of evaporation above and below the optimum water content. It is apparent, therefore, that the true significance of optimum water content is that particular content at which the soil can be put into the best possible condition for plant growth. The plant can then best draw its needed water from the soil because all the other factors making for good growth are also at their best. Moreover, an increase in water content in excess of the optimum generally produces a greater detrimental effect on the plant than a decrease below the optimum.

Furthermore, it should be borne in mind that practical men in bringing a soil to optimum water content judge when this point is reached by the appearance and " feel " of the soil; i. e., by the physical condition into which it can be brought, and not directly by any plant phenomenon. There is a widespread impression that the optimum water content for any one soil varies for different plants. That is, the *physiological* optimum, as determined by the plant, may not coincide with the *physical* optimum, as determined by the soil properties. While this may be true for certain exceptional cases, it is erroneous as regards the majority of common field crops, since the water content that makes for the best physical condition of the soil is as a necessary consequence the best for plant growth. Other evidence from experiments on wilting will be given in detail in support of this view. The available evidence seems to be conclusive that the problem of water supply and optimum water content is fundamentally a soil problem and incidentally a plant problem.

Another point which this investigation has brought out in a striking way is the " hysteresis " observable in the volume change when a soil is alternately wetted and dried out. This process results in a natural packing of the soil and is seriously detrimental to the maintenance of good tilth if the extremes of moisture content reached are wide apart. The causes for and mechanism of this process have been made clear by the experiments here recorded.

The importance in general farming of having a proper moisture content in the soil before plowing or other cultural operations is well known, although not always so well observed. It is regrettably common to find cases where the soil has been worked while too dry, and even more so are the cases where a soil has been worked while too wet, entailing disastrous results, requiring even years for rectification. These latter are the most baffling cases which the soil expert encounters.

The usual practice in irrigation gardening and greenhouse work of adding an excessive amount of water, so as to be on the " safe side," is far from the ideal soil management, and the working out of a better and at the same time an economical system of maintaining the water content constant, or approximately so, should be the aim of practical workers in these fields. It is believed that the data brought out in this bulletin will be of material assistance in understanding the phenomena involved in these difficult practical problems and in devising methods for the treatment and amelioration of lands which have been improperly handled.

In the course of this investigation a number of special methods and forms of apparatus were devised which it is believed will have a value not only for future investigation, but as a desirable part of the equipment of a laboratory for student work. It has been deemed well, therefore, to give quite complete and detailed descriptions, and to this end the methods and apparatus are described and illustrated in a special chapter at the end of the bulletin, and only brief references to them are given in the text describing the investigations.

PENETRATION AND COHESION.

PREVIOUS WORK.

A property of the soil of recognized agricultural importance is *cohesion*, or the force with which the soil particles cling one to another. The previous work on penetration has been usually incidental to investigations of cohesion. This property has been studied because it is a determining factor of the ease of tillage and because it gives a measure of the physical condition of the soil and its variation under different treatments. In these studies two methods have been employed. In the one the crushing strength of cylinders of soil has been taken as a measure of the binding together, or cohesion, of the soil particles; in the other the "firmness" of the soil, which is due to its cohesion, has been determined by the resistance offered to the introduction of a sharp instrument. These latter investigations have been regarded of especial value in showing the relative resistance of different types of soils to tillage and root penetration.

Volker [a] applied the penetration method to actual measurements in the field, without, however, obtaining definite results. A penetration method was used by Meyer [b] in which four pegs fastened to the corners of a square were forced a definite distance into the soil by weights placed on the square surface. The crushing method was used in an investigation by Schübler,[c] who molded damp samples of soil into rectangular prisms. The samples were then either allowed to dry in the form or were removed while still damp and dried in the air or at a high temperature. The apparatus used to determine the crushing strength of the samples consisted of a beam supported on a fulcrum about one-third the distance from one end. On the long arm of this lever was hung a scale pan to which weights could be added gradually. At the opposite end of the beam was a counterpoise that balanced the scale pan and beam. On the long arm, a short distance from the fulcrum, a blade was fastened, free to move in the vertical plane of the beam. The dried soil sample was placed under this blade and weights added to the scale pan until the soil was either cut or crushed by the knife. The weight added was taken to represent the cohesion of the soil. The highest absolute cohesion value, that for pure clay, was taken as 100 and the other measurements compared with this. The series of relative values obtained for the different soils is shown in Table I.

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[a] Neue Moglinische Annalen der Landwirtschaft, 4, 119 (1818); ref. in Puchner, Forsch. auf dem Geb. Agr.-Phys., 12, 196 (1889).

[b] Anlage zur Flora des Königreichs Hannover (Göttingen), 307 (1822).

[c] Grundsätze der Agrikulturchemie, Leipzig, 2, 74 (1838).

TABLE I.—*Cohesion of dry soils, according to Schübler.*

Soil.	Cohesion of dry soil compared to clay.	Soil.	Cohesion of dry soil compared to clay.
Pure clay (kaolin)	100.0	Humus	8.7
Clay soil	83.3	Garden soil	7.6
Fertile clay	68.6	Gypsum	7.3
Barren clay	57.3	Calcareous soil	5.0
Hofwyl soil	33.0	Calcareous sand	.0
Jura soil	22.0	Quartz sand	.0

This table shows that clay in the dry form has a relatively high cohesion, while humus and lime soils are low, and sand does not bind together at all. By comparing some of the values obtained for the above soils with their mechanical analyses it was shown that in the clay soils the presence of humus or sand greatly reduces the cohesion.

This method is of interest in showing the binding qualities of very dry soils, yet it is open to the objection that the results obtained by it do not give reliable data for soils under ordinary cultural conditions. It is rare for field soils to dry out to an extent comparable with the condition reached in this method; and it will be pointed out later that the relative values for the cohesion of different soils vary with the quantity of water present. The table shows further that the cohesion value of sand is zero, which means that in drying out the sand samples did not retain their form. If the measurements are to give a basis of comparison for the ease of working the soils in the field, such a value is of course meaningless. A method which depends on an unsupported soil column is evidently too wide a departure from field conditions.

It is apparent that measurements of soil cohesion are not of great agricultural interest unless they take into account the variable quantity of water in a soil at different times, since this quantity plays a most important rôle in determining all of its physical properties. Extensive experiments in soil cohesion taking account of this factor were made by Haberlandt,[a] in which he measured cohesion by the crushing strength of cylinders. He also divided some of his soil samples into three fractions, depending on the size of the grains, and in this way he was able to study the relation between soil cohesion and size of the particles. In the method as first used by him he molded cylinders of the soil in a glass tube one end of which was covered by a thin cloth. The cylinders and the glass tube were dipped in water to the depth of 1 centimeter and the soil allowed to take up moisture freely. The soil column, when removed from the glass tube, was 2 centimeters in diameter and 3 centimeters high. The cylinder was then allowed to dry until it had attained the desired moisture content, when the crushing strength was determined by placing a glass vessel on the top of the column and pouring in water until the soil gave way. From the weight of the vessel and water the value for the crushing strength was obtained in grams. The results for one soil are given in Table II.

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[a] Wissenschaftlich praktische Untersuchungen auf dem Gebiete des Pflanzenbaues, Wien, 1875, Vol. 1, p. 22.

TABLE II.—*Moisture-cohesion relations, according to Haberlandt.*

Grade of particles.	Moisture content.	Weight required to break down soil cylinders.
	Per cent.	*Grams.*
Coarse	32.6	120
	19.8	320
	13.1	725
	7.7	290
	2.4	170
Medium	25.9	225
	19.2	265
	16.8	500
	3.1	1,115
	1.2	1,080
Fine	33.4	450
	25.8	1,150
	7.0	1,900
	4.2	2,400
	1.9	4,200

From Table II it will be seen that the strength with which the particles are held together is greatly dependent on the moisture content of the soil. In two of the samples the cohesion value reached a maximum, indicating that in these soils a certain water content was of particular significance in regard to the cohesion. The soil with the finest particles became bound together more closely as it dried out, which is in agreement with the results of other investigators.

In another experiment Haberlandt studied the effect of mixing various quantities of sand and of moor soil with the sample of soil which was used in the previous experiment. As the percentage of sand increased the resistance to crushing diminished. This was likewise true of mixtures of the same soil with the moor soil.

In a later investigation Haberlandt[a] molded cylinders of the soil in a glass tube in the same way as before, and in addition to determining the crushing strength he measured the resistance to breaking under a transverse load, by placing the soil cylinder across two parallel horizontal supports 6 centimeters apart. Midway between the supports a scale pan was suspended from the soil cylinder, and weights were added continually until the soil column gave way. The weight required was taken as a measure of the "absolute" firmness of the soil. The pieces of the broken soil column were cut down to the desired size and a measurement of the "relative" firmness was made by crushing the sample in the same manner as before described. Measurements were made on twelve different soils in which the values for "absolute" firmness varied from 115 to 3.5 and for "relative" firmness from 9,000 to 700. Compared by either method the soils fell in practically the same order.

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[a] Forsch. auf dem Geb. Agr.-Phys., 1, 148 (1878).

The investigation was further extended by Haberlandt to determine the change in cohesion upon the addition of small amounts of charcoal and lime. The results are given in Table III.

TABLE III.—*Effect of lime and charcoal on cohesion, according to Haberlandt.*

Mixture.	Cohesion.
	Kilograms.
Untreated soil	31.4
Soil with 1 per cent charcoal	20.0
Soil with 1 per cent lime	8.9

The cohesion was reduced 36 per cent by charcoal and 72 per cent by lime. From his various experiments Haberlandt concluded: (1) The cohesion of different soils is widely different; (2) the cohesion depends on the size of the particles; (3) the cohesion of the soil is greatly diminished by the addition of lime, and this has a great influence in determining the ease with which soils can be worked in the field; (4) at some moisture content the cohesion is least for every soil. This last conclusion Haberlandt considered of great importance as bearing upon the question of the ease of working the soil in the field.

An extensive and valuable contribution to the literature of soil cohesion and penetration was made by Puchner,[a] who obtained values for "absolute" and "relative" firmness, both by the method of penetration and by a method similar to that of Haberlandt. The apparatus by which Puchner measured the penetration of soils consisted of a vertical shaft running through a metal guide. On the lower end of the shaft was fastened a penetrating knife blade 2 centimeters broad and 1 centimeter high, the angle of the cutting edge being 13°. The upper end of the shaft carried a scale pan to which weights were added directly until the blade was forced a required depth into the soil. The unloaded shaft and scale pan were counterpoised by a weight running over a pulley. By means of a pestle the dry soil sample was packed into a dish having a perforated bottom to permit of saturation with water taken up by capillarity. This amount of water was taken to represent the total water capacity of the soil, or 100 per cent moisture content. The samples were then allowed to dry until they reached the moisture content desired, when the penetration was measured by the apparatus just described.

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[a] Forsch. auf dem Geb. Agr.-Phys., 12, 195 (1889).

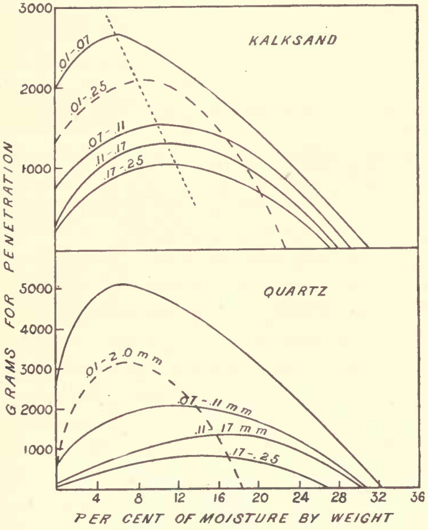

Fig. 1.—Influence of size of soil particles on penetration-moisture results for calcareous sand and for quartz, according to Puchner.

The influence of changing moisture content and that of size of particles on penetration were studied. For this purpose he used quartz sand separated into seven divisions, varying from 0.01 millimeter to 2 millimeters in diameter. The cohesion of these seven samples and a sample composed of all sizes was measured with varying water content. Experiments were also made on a calcareous soil (Kalksand), which was divided into four divisions, ranging from 0.01 to 0.25 millimeter. The results of these experiments are plotted in figure 1, the weight in grams necessary to force the blade the required distance into the soil being plotted as ordinate and the moisture content in percentage of dry weight as abscissa. The same abscissas hold for both the "Kalksand" and quartz curves. The numbers on the curves represent the limiting sizes of the particles. In order further to distinguish the curves representing the composite samples, they have been drawn in dotted lines. From these curves it is readily seen that the penetration values are greater for the finer particles and that the values for the composite samples lie between the extremes.

All these curves exhibit a maximum penetration value, from which it is evident that as the water content changes there is a corresponding change in at least this physical property, and that this particular water content has a special significance. As the size of particles varies the position of the maximum changes. In the case of "Kalksand" this has been indicated by drawing a straight dotted ine through the maxima. In the case of the quartz curves the maxima do not seem to bear so simple a relation to each other; this may be due to the fact that the composite sample contains many large particles (2 millimeters). Although there were seven divisions for quartz, only four of the corresponding curves are shown in the figure, since the curves for the larger sizes lie too close to the axis abscissas to be conveniently plotted.

The relation of penetration to changing moisture content was studied by Puchner with certain principal soil constituents (quartz, humus, and clay), and cohesion values were obtained for the pure substances and for their mixtures. In this work the measurements were limited to one range of particles between 0.01 and 0.14 millimeter. These results have been plotted in figure 2. The curves for kaolin and quartz, humus and kaolin, and quartz and humus are drawn in separate divisions and each has its own set of ordinates.

In the case of kaolin and the mixtures in which kaolin predominates the force necessary for penetration increases steadily as the soil dries out. In the other samples the penetration curves show again a maximum point. The curves are also interesting, since the absolute values for penetration of the pure substance and of mixtures may be compared directly.

In discussing the value of cohesion measurements made on dry samples alone as indicating the physical condition of agricultural land, it was pointed out that the results so obtained were likely to be misleading, since under field conditions we seldom have to consider a dry soil. The truth of this will become apparent on examining the curves. Taking, for example, the case of humus and kaolin in the dry condition, the cohesion values vary in the different samples from about 500 to 12,000 grams. Under favorable cultural conditions the mixture "1 humus+2 kaolin" would probably contain about 35 per cent water, while "2 humus+1 kaolin" might contain from 20 to 40 per cent; the pure humus would ordinarily contain from 70 to 90 per cent. At these moisture contents, which would represent fair field conditions, the cohesion values would not be very widely different.

In his experiments Puchner made observations on many other factors relating to penetration, such as the influence of "single grain" and "crumb" structure, addition of chemicals, plant covering, frost, etc., to some of which reference will be made later. He also made quite as complete a study of soil cohesion by measuring the crushing strength of cylinders of his soil material, from which he obtained the same results and reached the same general conclusions, as follows:

(1) The cohesion of the soil, i. e., the force with which the soil particles are bound together, depends on the physical constitution of the soil, on the moisture content, and on the presence of various salts.

(2) Of the different soil constituents, clay has the greatest binding strength, while that of quartz, humus, and lime is less. The cohesion of the soil will therefore depend on the relative proportions of the different materials.

(3) The influence of water on the cohesion of soils is of great importance. In clay and clay earth the cohesion is greater as the water content diminishes, while in humus, quartz, and lime the soil particles are most strongly held together at a medium percentage of water.

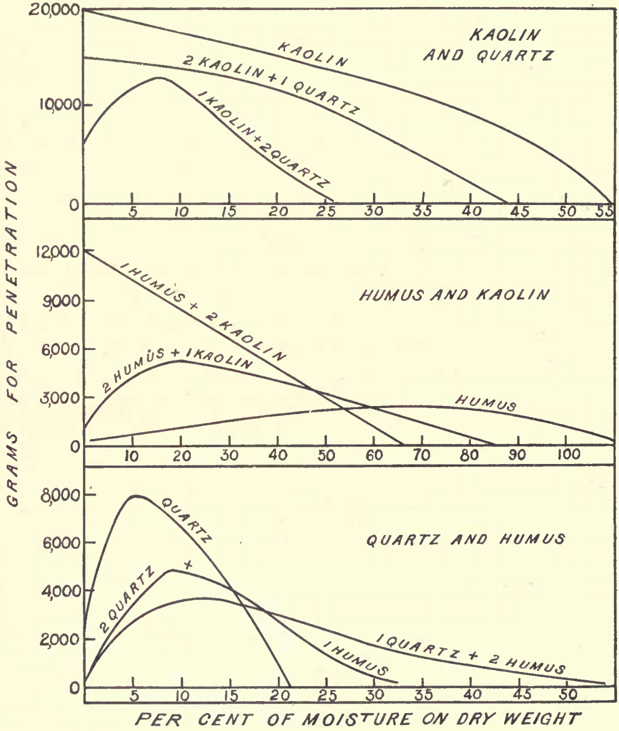

FIG. 2.—Penetration-moisture results for different soil components and mixtures of them, according to Puchner.

(4) The cohesion in any soil depends on the internal arrangement of the particles. It is greater in a "single grain" structure than in the "crumb" structure. If the soil particles are pressed together by an external force there results a proportional increase in the cohesion.

(5) Under otherwise similar conditions the binding strength of the soil is greater under crops than in fallow.

(6) The freezing of the soil greatly raises the absolute firmness.

(7) On the addition of lime the cohesion of clay is reduced under all moisture conditions, while the addition of potassium hydroxide and potassium carbonate increases the cohesion when the soil is dry, but reduces it at higher moisture content.

(8) In a consideration of the moisture condition most favorable for working a soil and best suited to placing it in most favorable mechanical condition, the question of cohesion should not enter, since with a medium water content (somewhere about 40 per cent of the total water capacity) the cohesion of most soils is at a maximum, and the soil can then be worked more easily into a crumbly condition. It is desirable to obtain the crumb structure, which is the best physical condition of the soil—i. e., the condition most favorable for crop production—even at the expense of greater labor.

It is quite evident from the work of other investigators that the cohesion or binding power is quite different for different soils and that it determines the penetrability. It is a matter of particular interest that the penetrability is closely connected also with the amount of moisture in soils. In order to investigate the influences of water on the physical condition and on the productiveness and apparent fertility of soils, a further study on penetration has been made.

RELATION OF PENETRATION TO MOISTURE CONTENT.

Object of experiments.

Unlike previous investigations in soil penetration, these measurements were not made primarily to study soil cohesion or to determine the resistance offered by various soils to cultural treatment. The purpose was rather to determine what constitutes a favorable physical condition for plant growth and how water affects this condition. It was assumed that the soil could be put into a most favorable condition as a cultural medium and that penetration measurements could be taken tentatively as an index of this state.

These considerations had an important bearing on the development of the methods used. It was pointed out by Puchner that a soil can best be put into a crumbly structure when it contains a medium amount of water. The importance of a crumb structure as a soil condition has long been known to agricultural men, and is earnestly sought in good agricultural practice. The ability of a soil to build a crumb structure or to form itself into aggregates is an important factor, determining the value of that soil as a medium for plant growth. The penetration work in previous investigations of soil cohesion has not been conducted under conditions best suited to plant growth. In fact the experimental procedure usually put the soil samples in a condition much worse than obtained in field practice. The soils were packed when dry, often with a pestle, so that the individual grains were worked into very close contact with each other, and the soils were then completely saturated with water, the samples being thus packed still closer. The desired water contents at which measurements were made were obtained by letting the saturated samples dry out. Such a procedure could hardly be said to duplicate field conditions. In order to study the influence of water upon the soil as a cultural medium it was desired to put every sample of soil into the most favorable state possible.

Experimental methods.

Neither absolute values for penetration, nor the comparison of these absolute values for different soil types were attempted; but rather the aim was to determine the variation in the penetration values for one particular soil at different moisture contents. Furthermore, a comparison of the penetration values for different soils can not be made, on account of frequent changes in the apparatus during the course of the investigation. No such variation as this, however, occurs during a set of measurements on any one soil sample, and these results are strictly comparable with one another.

In this problem one of the most serious difficulties encountered was so to control the handling of the soil sample and its packing that an agreement in results could be obtained between duplicate experiments. The difficulty in regulating the packing was rendered greater by the fact that the soils were to be examined in a loose condition, in which state even slight changes in the packing force produce large variations in the results. In studying the change of penetration with varying water content it was desired that all soil samples should have the same treatment. This it was impossible to do so long as the samples were worked by hand, and it was only possible when the process of packing was made purely mechanical. To this end a power-driven shaker (see fig. 27, p. 60) was devised, in which the soil samples were run through a coarse screen, after which they fell a definite distance through a funnel into the dish in which the penetration measurement was to be made. Since the screening was mechanical and the same in each case, the packing could be changed by varying the height through which the soil fell.

The apparatus for measuring the penetration (see fig. 30, p. 64) consisted of a long lever arm from the end of which was suspended a sharp conical tool of steel, free to swing in the vertical plane of the lever beam. This tool was forced a definite distance into the soil sample by weights added gradually to the middle of the beam. The unloaded beam and attachments were balanced by a counterweight hung beyond the fulcrum on the opposite end of the lever.

In making a penetration measurement the procedure followed was to make up a soil sample to about the desired moisture condition. The sample was run through the screening machine into the dish in which the penetration measurement was to be made. This dish was large enough so that several measurements were made on each sample.

the mean of which was taken to represent the final value. The data for the complete variation of the moisture content were usually obtained by starting with air-dry soil. After the penetration value for this sample was obtained, enough water was added to the same lot of soil to increase the moisture content by a few per cent. This sample was in turn screened and measured, as before. The moisture content was thus gradually increased and measurements taken until the soil became too moist to work. The process could be reversed with equal success by letting the wet soil dry out to the desired point as long as the sample was screened at the same moisture content for which the penetration was determined. The amount of water present in the soil at each measurement was determined by drying a sample of the soil at 110° C. and calculating the moisture content to the dry weight, since this method gives moisture values which for any one soil are directly proportional to the actual amounts of water present. This method does not, however, give any idea of the moisture relations when comparison is made between different soils.

Results for Podunk fine sandy loam.

The first measurements of penetration were made for Podunk fine sandy loam, the mechanical analysis of which is given in Table IV.

TABLE IV.—*Mechanical analyses of Podunk fine sandy loam.*

Name of division.	Limits of size.	Percentage.	Name of division.	Limits of size.	Percentage.
	Millimeters.			*Millimeters.*	
Fine gravel	2.0 —1.0	0.0	**Very fine sand**	0.1 — .05	30.4
Coarse sand	1.0 — .5	.0	**Silt**	.05 — .005	18.8
Medium sand	.5 — .25	1.0	**Clay**	.005— .0	2.2
Fine sand	.25— .1	47.6			

This soil is seen to consist very largely of fine sand and very fine sand, along with considerable silt. It proved to be a soil particularly well adapted to an investigation of this kind, being very easy to work and not becoming sticky when water was added to it. In the air-dry condition it was found to hold about 0.3 per cent of water, and when completely saturated by letting water rise by capillarity into short columns it held about 30 per cent. The results of a series of penetration measurements on this soil are given in Table V.

TABLE V.—*Penetration-moisture relations for Podunk fine sandy loam.*

Moisture content.	Weight required for penetration.	Moisture content.	Weight required for penetration.
Per cent.	*Grams.*	*Per cent.*	*Grams.*
0.36	112	7.9	33
.92	73	10.5	38
3.9	28	13.4	42
5.8	28		

These results are shown graphically in figure 3, where the water content is measured on the axis of abscissas and the weight required for penetration on the axis of ordinates.

It can be seen from this that when the soil is put into the loosest possible condition the penetration measurements give a minimum between 4 and 6 per cent of water. This would indicate that as the moisture in the soil changes there is a definite variation in this physical property, and that one particular range of water content seems to have a special significance. It makes no difference in the result whether the water content be changed by adding water to the soil or by drying out a wet soil, for at one and the same moisture content the penetration value is a minimum.

As was pointed out in the introduction, there is a moisture condition in each soil which is recognized as the "optimum" water content, and is determined by the "feel" of the soil. To determine whether there is a relation between the critical amount of water as found in the above penetration work and this optimum water content, several samples of Podunk fine sandy loam, containing different amounts of moisture, were made up to optimum condition by practical greenhouse men. When the moisture determinations of the samples were made they were between 5 and 7 per cent of water, thus suggesting that the minimum in the penetration curve has a casual connection with the optimum water content, a quantity which up to this time has been purely arbitrary.

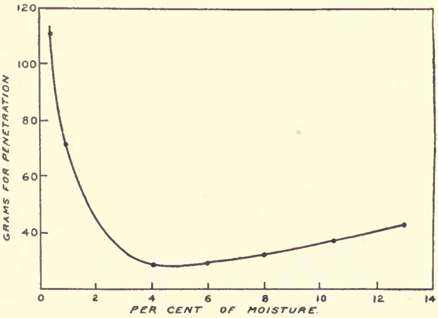

FIG. 3.—Penetration-moisture results for Podunk fine sandy loam.

Another set of penetration-moisture results, obtained in a similar manner except that the packing was somewhat greater, is given in Table VI.

TABLE VI.—*Penetration-moisture relations for Podunk fine sandy loam.*

Moisture content.	Weight required for penetration.
Per cent.	*Grams.*
0.3	178
2.6	53
6.0	48
11.6	54

These results are like the others in that they show a minimum at about 6 per cent of moisture content.

In working this soil preparatory to the measurements a great difference was noticed in its behavior as the amount of water was changed. The air-dry sample was of course in poor condition for agricultural purposes and was quite difficult to work because of the dusty nature and the compact state into which it settled. The addition of very little water produced a great change, as might have been predicted from the penetration curve; and although the soil was too dry for agricultural purposes, it was no longer dusty, seemed much lighter, and it screened and packed better. The soil sample giving the least penetration value responded most readily to working; it screened well, felt damp, light, and of an even texture. Beyond this point the soil began to feel wet and to show the effects of what might be called "free water"—i. e., water which does not seem to be an integral part of the soil. At 10 per cent water content the soil was still in fairly good condition, although it screened rather slowly, and beyond 14 per cent it could not be worked because of the difficulty of screening the wet soil. At this point it was evident that the soil was too wet for good plant growth. Although this method does not permit a study of soil condition in the neighborhood of the saturation point, it does allow sufficient variation to cover the range of soil moisture usually met under growing conditions, a range extending well above and below the optimum water content.

The penetration values according to this method form an interesting comparison with the plant growth on soils containing varying quantities of moisture. In the air-dry condition the soil is not able to sustain crops. When enough water has been added to the soil to enable it to support plant life, the penetration values drop very rapidly and are of the same order of magnitude as found at the minimum point. Beyond the minimum the penetration for Podunk fine sandy loam rises very slowly, which may be interpreted to mean that the physical condition of this soil changes but slightly over a range of several per cent, for the soil remains in very fair condition for plant growth over quite a wide range above 6 per cent of moisture.

It will be remembered that in his work on soil cohesion Puchner obtained maxima in his penetration-moisture curves, while the results just described showed minima. Puchner attributed his maximum values to an increase in the soil cohesion due to the presence of a definite amount of water in the soils. He also pointed out that this particular amount of water in the soil was most favorable for the formation of floccules or soil aggregates and the attainment of a crumb structure, due to this same increased cohesion. This appears to connect his observations with those here recorded and to show that the same forces which caused a maximum under the one method of procedure operated under a very different method to give a minimum. In order to test this point, a penetration-moisture study was made on Podunk fine sandy loam under conditions similar to those of the Puchner method. The results obtained are given in Table VII and graphically represented in figure 4. In order to make this result more easily comparable with other penetration results, we have included in the figure, using the same abscissas, a curve obtained for the same soil by the regular method of loose packing. Each curve, however, is given with its own ordinates. Although the penetration value for the critical point exhibited by the maximum is over one hundred times as large as the value given by the penetration at the minimum, and although the methods are widely different and represent very different conditions of internal arrangement of the soil particles, the agreement of the critical points in regard to the water content of the soils is very striking indeed. From this it is evident that in a soil some particular water content is of marked importance in determining the physical character of the soil, which property is undoubtedly determined by the distribution of the water.

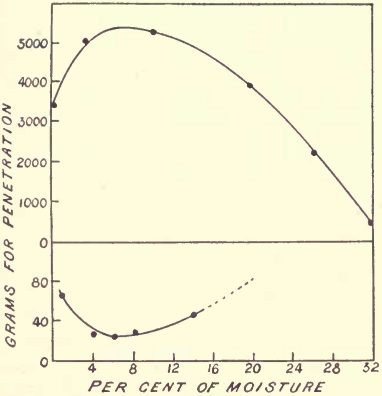

FIG. 4.—Penetration-moisture results for Podunk fine sandy loam by method of Puchner and by method of loose packing.

TABLE VII.—*Penetration-moisture relations for Podunk fine sandy loam, by the Puchner method.*

Quantity of water in soil.		Weight required for penetration.
Proportion of dry weight.	Proportion of total water capacity.	
Per cent.	*Per cent.*	*Grams.*
32.0	100.0	532
26.0	81.0	2,320
19.4	60.8	4,080
8.6	26.8	5,300
2.7	8.5	5,052
.0	.0	3,400

At the same time some experiments were made on the variation in the penetration-moisture relations when the soils were packed under different pressures. These results have a special interest in connection with the forms of the curves obtained by Puchner's method and by our method. In studying the effect of packing the soil, samples of Podunk fine sandy loam were prepared in the regular manner of loose packing, except that before the penetration measurement was made the desired pressure was applied to the surface of the soil by means of an apparatus designed for that purpose (see p. 62). The results of these measurements are given in Table VIII, and shown graphically in figure 5. The amount of the pressure per square centimeter used in packing the soil is given on each curve.

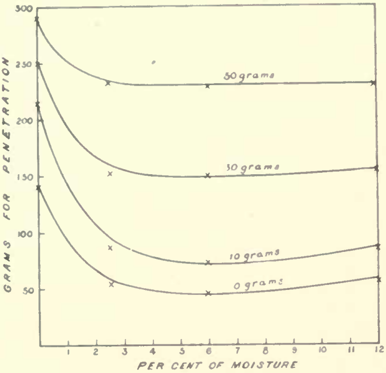

FIG. 5.—Penetration-moisture results with different packings.

TABLE VIII.—*Penetration-moisture relations for Podunk fine sandy loam, packed under different pressures.*

Packing force per square centimeter.	Moisture content.	Weight required for penetration.	Packing force per square centimeter.	Moisture content	Weight required for penetration.
	Per cent.	*Grams.*		*Per cent.*	*Grams.*
0 gram	0.0	178	30 grams	0.0	250
	2.6	53		2.6	155
	6.0	48		6.0	150
	12.2	51		12.2	154
10 grams	.0	237	50 grams	.0	291
	2.6	84		2.6	232
	6.0	72		6.0	230
	12.2	82		12.2	230

Although the pressures applied are not large and do not raise the penetration values anywhere near the point reached by samples measured according to Puchner's method, yet there is a well-defined tendency for the curves to flatten out as more pressure is applied. There is much less difference between the penetration values of the minimum and the dry state in the sample packed under 50 grams than there is in the sample packed under 10 grams pressure. The difference in the results obtained in the two penetration methods discussed is obviously one of packing. It would seem that upon increasing the pressure used in packing the loose samples a series of curves would be obtained ranging from those by our method, showing a minimum, to those by the Puchner method, showing a maximum. It was not deemed advisable at the present time to investigate this point further.

Results for Miami black clay loam.

Having found the above results for a sandy soil of low water capacity and poor in organic matter, the same method of study was applied to the Miami black clay loam, a soil of widely different character, a silty soil rich in organic matter, having a large capacity for water. The mechanical analysis of this soil is given in Table IX.

TABLE IX.—*Mechanical analysis of Miami black clay loam.*

Name of division.	Limits of size.	Percentage.	Name of division.	Limits of size.	Percentage.
	Millimeters.			*Millimeters.*	
Fine gravel	2.0 -1.0	1.2	Very fine sand	0.1 -0.05	6.2
Coarse sand	1.0 - .5	7.6	Silt	.05 - .005	53.4
Medium sand	.5 - .25	3.9	Clay	.005- .0	11.6
Fine sand	.25- .1	16.1			

The total water capacity of this soil is about 60 per cent, and in the air-dry condition it ordinarily contains about 8 per cent of moisture. When this soil was made up to optimum water content by field methods it was found to contain from 35 to 40 per cent of water.

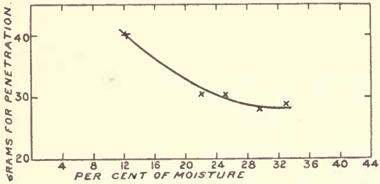

FIG. 6.—Penetration-moisture results for Miami black clay loam.

A penetration-moisture curve was made for Miami black clay loam when the soil was put each time into the loosest possible condition, the method being the same as already described for Podunk fine sandy loam. The results are shown graphically in figure 6.

When water was added to a comparatively dry sample the penetration value dropped to a minimum at 32 per cent moisture content. Enough water was added to the 32 per cent sample to increase the water content by several per cent, whereupon the soil proved too sticky to screen well. At 32 per cent the soil was in excellent condition, but on account of its clayey nature a few per cent of water caused a great change in the "workability." From this curve it is evident that as water is added to the dry soil, the cohesion is increased and the soil can be worked into aggregates. When the cohesion of the soil is greatest, as evidenced by a minimum in the penetration curve, the soil is in excellent physical condition.

Results for Leonardtown loam.

The next soil studied was quite different from those previously described, being a light-colored soil containing considerable clay and little organic matter, becoming rather sticky when wet, and on drying setting in a hard condition. The optimum water content for this soil was found to lie at about 15 per cent, a value midway between the optimum water content of the Podunk fine sandy loam and that of the Miami black clay loam. In the air-dry condition the soil contains about 1.3 per cent of water and when saturated holds some 34 per cent Several concordant sets of penetration results were obtained for this soil. Despite its tendency to become sticky when wet, it was possible to carry the penetration curve some distance beyond the optimum water content. Table X and figure 7 show the results of one set of measurements. The curve drops to a well-defined minimum at about 15 per cent of moisture, which is also the optimum water content.

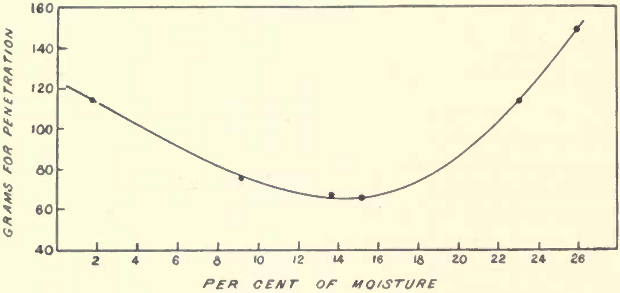

FIG. 7.—Penetration-moisture results for Leonardtown loam.

TABLE X.—*Penetration-moisture relations for Leonardtown loam.*

Moisture, calculated on dry weight of soil.	Weight required for penetration.	Moisture, calculated on dry weight of soil.	Weight required for penetration.
Per cent.	*Grams.*	*Per cent.*	*Grams.*
1.7	115	15.2	66
9.1	75	23.1	115
13.7	68	25.9	150

It was pointed out in the case of Podunk fine sandy loam that the form of the penetration curve might serve as an index to the character of the soil, and that for several per cent beyond the optimum water content the penetration curve rose very slowly, indicating that the physical properties change slowly and that the soil remains in fairly good agricultural condition. The penetration curve for

Leonardtown loam rises sharply, indicating a more marked change in the physical condition of the soil. Here also the curve corresponds to the field observations, for the favorable soil condition existing at 15 per cent of water rapidly disappears with a slight increase of water content. Further data on penetration for this soil are given in Tables XXIII and XXIV.

Results for Muck.

The next soil was studied as a check upon the conclusions reached in the previous work because it is an extreme soil type, being composed largely of organic matter and having a high water content. The mechanical analysis of this soil is not presented, as it would give little indication of the soil texture owing to the large quantity of organic matter present. In the air dry condition this soil ordinarily holds about 45 per cent of water, and when saturated some 220 per cent. The soil is in good condition for agricultural purposes over quite a wide range of moisture content, and it would be difficult to assign a close limit for the optimum water content as determined by the ordinary field method; however, it may be considered as between 120 and 140 per cent. The penetration measurements were made in the usual manner, the results being given in figure 8. From this it is seen that the penetration value reaches a minimum at about 120 per cent of moisture, which agrees well with the optimum water content.

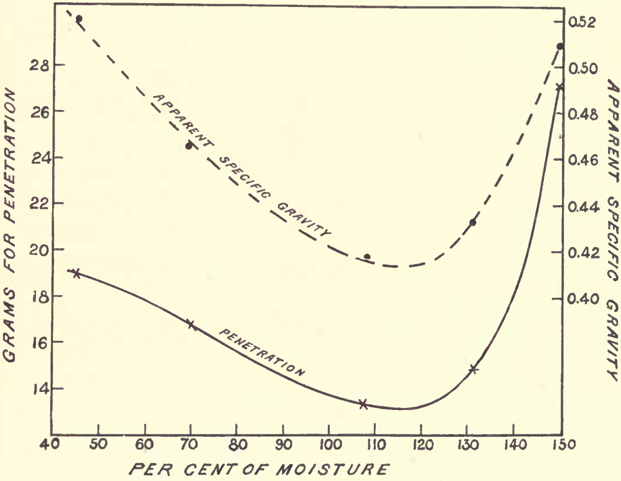

FIG. 8.—Penetration-moisture and apparent-specific-gravity-moisture results for Muck.

APPARENT SPECIFIC GRAVITY OR VOLUME.

PREVIOUS WORK.

In 1838 Schübler[a] studied the volume changes of soil by drying out wet samples until the weight no longer decreased. Representing the original volume as 1,000, he gives the volume to which the soils contracted on drying. In this way a comparison was obtained between different soil types. The results are shown in Table XI.

TABLE XI.—*Volume changes of soils on drying, according to Schübler.*

Material.	Percentage of original volume.	Material.	Percentage of original volume.
Quartz sand	100.0	Clay	88.6
Calcareous sand	100.0	Ordinary field soil	88.0
Gypsum	100.0	Fertile garden soil	85.1
Slate marl	96.5	Magnesium carbonate	84.6
Calcium carbonate	95.0	Kaolin	81.7
Potters clay	94.0	Humus	80.0
Clay loam	91.1		

The diminution of volume on drying was determined for six soils by Wolff,[b] who measured the change by means of a graduated cylinder. The influence of the size of the particles on the volume changes in soil was first studied by Haberlandt.[c] He used twelve soil samples, each of which was divided mechanically into ten separations. From the change in volume of the different soils and the water capacity, humus content, and mechanical analysis, conclusions were reached regarding the influence of different soil constituents on the volume changes. The experimental method consisted in measuring the change in volume of soil cylinders made from the damp earth. Haberlandt came to the following conclusions:

(1) The volume change which different closely packed soils undergo in drying out from a wet condition varies from 0 to 20 per cent of the original volume.

(2) Such volume changes are measured best in closely packed soils; loose soils are not well suited to measurement.

(3) Of the soil constituents humus has the most influence on volume change.

(4) It is probable that the volume changes of soils bear a linear relation to the fineness of the particles; yet this is only the case when these fine particles all have the same power to swell.

The volume changes due both to drying out and wetting were studied by von Schwarz.[d] He used four soil samples the mechanical analyses of which are given in Table XII. The volume changes are given in Table XIII.

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[a] Grundsätze der Agrikultur-Chemie, Leipzig, II, 82 (1839).

[b] Anleitung zur chemischen Untersuchung landwirtschaftlich wichtiger Stoffe, Berlin, 1899.

[c] Fühling's landw. Ztg., 7, 481 (1877).

[d] Erster Bericht über Arbeiten der k. k. landwirtschaftlichen Vers.-Stat. in Wein (1870–1877), p. 51.

TABLE XII.—*Mechanical analyses of soils used in volume studies by von Schwarz.*

Soil type.	Sands.				Suspended material.
	Coarse.	Medium.	Fine.	Very fine.	
	Per cent.	*Per cent.*	*Per cent*	*Per cent.*	*Per cent.*
1. Sand	0.0	96.34	3.11	0.55	0.55
2. Loam	0.0	19.87	31.70	30.39	18.04
3. Clay	0.0	0.0	0.0	4.53	95.47
4. Moor	Contained 82.6 per cent organic matter.				

TABLE XIII.—*Volume changes of soils on drying, according to Von Schwarz.*

Soil.	Decrease on drying.	Increase on wetting.
	Per cent.	*Per cent.*
1. Sand	0.0	0.0
2. Loam	17.0	19.2
3. Clay	29.8	42.4
4. Moor	60.2	....

An extended study of the volume changes on wetting and drying soils was made by Wollny.[a] In the apparatus devised by him for this study the soil samples were contained in a wide cup with a perforated bottom. This was surrounded by an outside dish so that the samples could be wetted by capillary water. On the surface of the soil rested a metal plate to which an upright rod was fastened. The weight of the rod and plate was counterbalanced by a weight running over a pulley. The upper part of the rod was notched so that it constituted a part of a rack and pinion that, on moving, revolved a pointer on a circular scale. The soil to be measured was packed into the containing dish in the dry state, the surface leveled, and the plate which moved the measuring mechanism was adjusted to the surface. By allowing the wet soil to dry, another measurement could be made. A measurement of the relation of volume change to size of particles on drying a soil gave the results in Table XIV.

TABLE XIV.—*Volume changes on drying soil separates, according to Wollny.*

Soil (quartz sand).	Size of particles.	Decrease in volume due to drying.
	Millimeter.	*Per cent.*
I	0.01–0.07	0.99
II	.07– .01	.17
III	.11– .17	.15
IV	.17– .25	.11
V	.25– .50	.0

From this table it follows that the change of volume in quartz sand is greatest for the finest material. Similar results were obtained when the dry soil samples were wet, although in this case the volume changes were greater, as can be seen from Table XV.

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[a] Forsch. auf dem Geb. Agr.-Phys., **20**, 1 (1897).

TABLE XV.—*Volume changes on wetting soil separates, according to Wollny.*

Soil (quartz sand).	Size of particles.	Increase in volume due to wetting.
	Millimeter.	*Per cent.*
I	0.01–0.07	8.01
II	.07– .11	5.09
III	.11– .17	1.25
IV	.17– .25	.78
V	.25– .50	.0

Measurements were made on drying and wetting the principal soil constituents—quartz, clay, and humus, and their mixtures. The quartz used in this work was the finest size, varying from 0.01 to 0.07 millimeter. Table XVI gives the values obtained both in drying and wetting the samples.

TABLE XVI.—*Volume changes of different soil constituents and their mixtures due to changing moisture content, according to Wollny.*

Soil mixture.	Decrease on drying.	Increase on wetting.
	Per cent.	*Per cent.*
Kaolin	39.92	36.92
Kaolin, 2 parts + quartz, 1 part	33.17	30.90
Kaolin, 1 part + quartz, 2 parts	20.63	19.28
Quartz	.99	8.01
Quartz, 2 parts + humus, 1 part	2.86	10.84
Quartz, 1 part + humus, 2 parts	4.58	14.07
Humus	5.39	15.92
Humus, 2 parts + kaolin, 1 part	23.63	25.22
Humus, 1 part + kaolin, 2 parts	35.19	32.79

From this it is to be concluded that the volume changes in a soil are greater the more clay there is present and less the greater the amount of quartz. The humus causes an increase in the volume change when mixed with quartz, but has an opposite influence in mixtures of clay.

A number of other factors that influence volume changes in soils were studied by Wollny, such as effects of hydrates and salts, the effect of the arrangement of the soil particles, and the effects of rainfall and freezing, to some of which further reference will be made in the following pages.

RELATION OF VOLUME TO MOISTURE CONTENT.

Object of experiments.

From the work on volume changes just reviewed it is evident that variations in volume of greater or less magnitude occur in all soils when wetted and dried, which changes are influenced by a number of factors. The relation between the magnitude of these changes had been well established for a number of soils and under a number of different conditions. In none of the work, however, is there any reference to the variation in volume with the variation in moisture content. What has been measured may be designated the "total" change, which represents the difference in volume between the saturated and the air-dry conditions. Whether all or the greater part of the variation occurs over the range of low percentage of water or near the saturation point, or whether it is equally distributed over the entire range of moisture variation, has not been determined. In studying the effect of different amounts of water as affecting the physical state of the soil and determining favorable conditions for plants, it is of particular interest to know whether special quantities of water have a determining influence on the physical properties.

Variations in water content have all been in one direction, from the wet to the dry state, since there is no satisfactory way of adding regular intermediate percentages of water to a soil and leaving it in place for measurement. A soil could of course be molded into any convenient shape, saturated with water and measurements on the volume of the sample made as the water content decreased, without in any way disturbing the soil sample. The parallel results obtained by Wollny in the measurement of the "total" volume change in wetting and drying out a sample, indicate that the determinations in drying out a sample will probably give a true idea of the nature of the changes occurring.

Experimental methods.

Several different methods were used to measure the change in volume, because it was desired to have check methods and because different soil samples did not lend themselves equally well to the same method. The contraction along one dimension was measured rather than the actual volume change. The assumption was made that the contraction was the same in all directions and from the linear change for unit length the percentage volume decrease was calculated from the formula $D=1-(1-x)^3$, where x represents the unit linear change.

In one method, which will be designated the "soil column method,"[a] a cylinder of soil was supported in an inclined position on a metal form made by sawing a brass tube in half, longitudinally. A cylindrical brass follower was brought in contact with the upper end of the soil column. As the wet soil column dried out and diminished in length the brass follower moved downward, and this movement was measured by means of a micrometer screw, reading to 0.001 centimeter.

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[a] For full description see p. 67 and fig. 32.

This same micrometer was used at a different time to measure the contraction of samples contained in vertical glass tubes (see p. 65 and fig. 31) where a follower was also used in connection with the soil surface. This method will be designated as the "glass-tube method."

A different micrometer screw, reading to 0.0001 centimeter, was used in another method, where the soil sample was held in a cylindrical dish (see p. 68 and fig. 33), through the perforated bottom of which the sample could be saturated with water. A brass disk was set on the surface of the soil and the micrometer point brought in contact with this. For convenience this method will be designated the "micrometer method." A cathetometer was used to follow the contraction in soil samples supported in containing vessels having perforated bottoms. The point of an upright shaft, supported by a disk resting on the surface of the soil, was focused on the cross lines of the cathetometer telescope and thus the variation in the height of the soil surface was followed. This method will be called the "cathetometer method."

As a further indication of volume changes the apparent specific gravity of the soil was measured by weighing a unit volume in the condition in which it was worked. These observations were made at the same time that the penetration work was being carried on. In determining these data for the various soil samples it was necessary to level off the dish carefully, weigh dish and soil, and divide the weight of the soil by the volume of the dish.

Results for Podunk fine sandy loam.

It has been shown above that at a certain percentage of water the penetration results indicate that it is possible to work the soil into a maximum "looseness," which amount of water corresponds to the optimum water content. This observation was further checked by measuring the apparent specific gravity of the soil—the results being given in Table XVII.

TABLE XVII.—*Apparent specific gravity-moisture relations for Podunk fine sandy loam.*

Moisture content.	Apparent specific gravity.	Moisture content.	Apparent specific gravity.
Per cent.		*Per cent.*	
0.36	1.31	7.9	0.665
.92	1.21	10.5	.722
3.9	.69	13.4	.777
5.8	.655		

These data are better illustrated by the curve in figure 9, from which it is seen that the variation of apparent specific gravity with moisture content corresponds closely with the penetration-moisture results. On account of the greater accuracy attainable by weighing, the data given by the apparent specific gravity variations are even more concordant than those given by penetration measurements, which are more difficult to make with accuracy on account of the influence of small irregularities in packing.

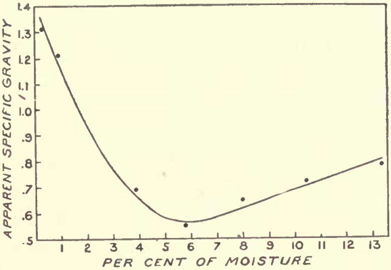

FIG. 9.—Apparent-specific-gravity-moisture results for Podunk fine sandy loam.

The apparent-specific-gravity data obtained in connection with the penetration measurements made when the soil was subjected to different packing pressures are shown by means of the curves in figure 10,

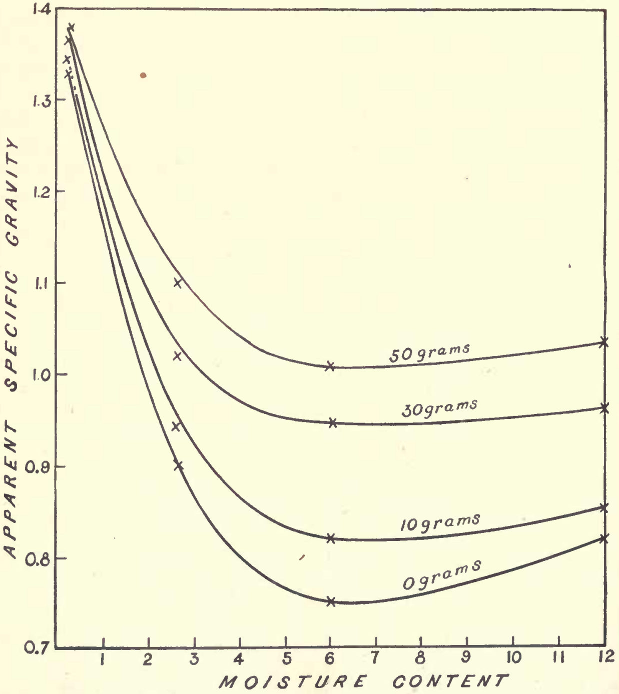

FIG. 10.—Apparent-specific-gravity-moisture results for Podunk fine sandy loam with different packings.

where the numbers on the curves represent the packing force per square centimeter. These curves are similar to the corresponding penetration curves, but they indicate more clearly the tendency to flatten out under increasing pressure due to the fact that the specific gravities of the dry samples are much closer together, so that the results of packing the loose soils at the optimum water content are more marked.

It can be readily seen from the work of Wollny on the "total" change of volume of soils that the measurement of the change of volume in sand with varying moisture content would present exceptional difficulties on account of the very small change of volume. When it is borne in mind that the volume is a cubical function of one length, the difficulty of obtaining accurate measurements on the linear contraction can be appreciated. In comparison with the readiness with which contraction measurements were made on some soils, the study of the volume change in Podunk fine sandy loam presented serious experimental difficulties. But these results were essential in order to compare the variations in this physical property with the changes in penetration and apparent specific gravity already given, and to complete a correlation of the individual properties that are dependent on the moisture content of the soil.

The results of a series of measurements on the volume changes in Podunk fine sandy loam as made by the micrometer method are given in Table XVIII.

TABLE XVIII.—*Volume-moisture relation for Podunk fine sandy loam.*

Moisture content.	Linear decrease.	Volume decrease.	Moisture content.	Linear decrease.	Volume decrease.
Per cent.	*Centimeter.*	*Per cent.*	*Per cent.*	*Centimeter.*	*Per cent.*
32.9	0.0	0.0	11.5	0.022	7.13
29.8	.006	1.98	9.7	.022	7.13
29.0	.007	2.19	8.2	.022	7.13
27.7	.011	3.6	6.8	.022	7.13
22.7	.021	6.87	6.4	.0225	7.13
18.3	.022	7.13	5.4	.0255	8.36
16.0	.022	7.13	3.7	.0255	8.36
12.2	.022	7.13	2.0	.026	8.40

From the table it will be seen that the saturation point at which the measurements were started was about 33 per cent moisture content. As the sample dried out there was a gradual decrease in volume until about 18 per cent of water was reached when the contraction had amounted to 7.13 per cent of the original volume. From this point on there was very little, if any, contraction in volume over many per cent decrease in moisture content. When the soil reached about 6 per cent moisture content, however, a more rapid volume decrease commenced. At 2 per cent of water the volume decrease had reached

8.4 per cent of the original volume. These data are shown in another form in figure 11, where the moisture content is platted as abscissa and the per cent volume decrease as ordinate.

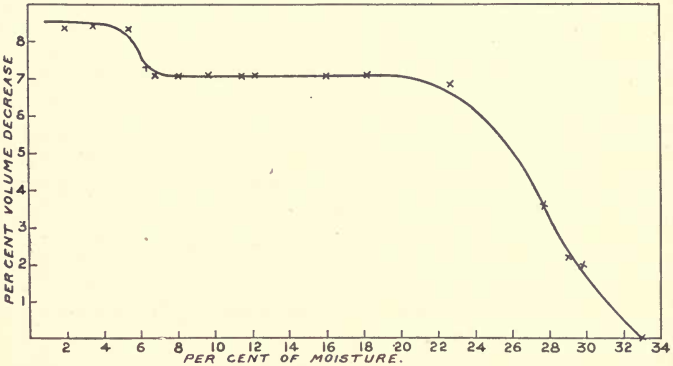

FIG. 11.—Volume-moisture results for Podunk fine sandy loam by the micrometer method.

In Table XIX and figure 12 is given a series of measurements made by the "glass-tube method," and these show the same variations as do the previous measurements.

TABLE XIX.—*Volume-moisture relations for Podunk fine sandy loam.*

[Length of soil column, 10 centimeters.]

Moisture.	Linear decrease.	Volume decrease.	Moisture.	Linear decrease.	Volume decrease.
Per cent.	*Centimeter.*	*Per cent.*	*Per cent.*	*Centimeter.*	*Per cent.*
23.8	0.0	0.0	5.9	0.023	0.69
17.7	.015	.48	3.0	.043	1.30
9.3	.016	.50	1.6	.043	1.30
7.4	.016	.50			

The total percentage decreases are not the same by the two methods. As was pointed out in the chapter on penetration, the "absolute" values of these changes have no significance, but only the relation between the water content and the property being studied. It is to be noticed, however, that the measurements by the latter method were not begun at 33 per cent, but at 24 per cent, and if a similar range be taken on the curve of figure 11 the total volume changes by the two methods more nearly approach each other. Considering the curves

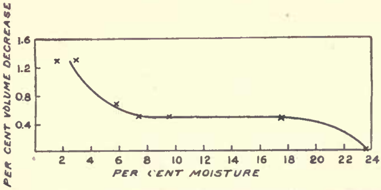

FIG. 12.—Volume-moisture results for Podunk fine sandy loam by the cathetometer method.

within the range of the moisture content covered in the penetration work—namely, 14 per cent to 0 per cent—it will be seen that from 14 to 6 or 7 per cent there is no appreciable change in volume in Podunk fine sandy loam, the loss of water over this range having no influence on the volume of the soil. In the neighborhood of 6 per cent, however, a change is noticeable, a loss of water beyond this point being accompanied by a diminution in the volume of the sample.

Thus, it follows that not only in the penetration but also in the aparent specific gravity a change occurs in the physical properties of the soil at about 6 per cent moisture content, which content is also the optimum. It is evident, therefore, that the optimum water content has an important physical significance and the work on volume contributes much to an understanding of the factors that operate at the optimum water content.

Results for Miami black clay loam.

Very satisfactory volume results were obtained in the measurements on the Miami black clay loam. The nature of the soil made it well suited to the soil column method of measuring volume change; because of its clayey nature and organic matter content it was able to retain the form of the soil column both in a very wet and a very dry condition. Further, the presence of the clay and organic matter caused greater volume changes, which added much to the ease of obtaining results.

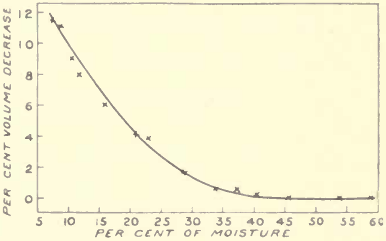

FIG. 13.—Volume-moisture results for Miami black clay loam by the soil column method.

A set of data obtained for Miami black clay loam on the volume changes with varying moisture content is given in Table XX and represented graphically in figure 13.

TABLE XX.—*Volume-moisture relations for Miami black clay loam by the soil column method.*

[Length of soil column, 14 centimeters.]

Moisture.	Linear decrease.	Volume decrease.	Moisture.	Linear decrease.	Volume decrease.
Per cent.	*Centimeter.*	*Per cent.*	*Per cent.*	*Centimeter.*	*Per cent.*
59.0	0.0	0.0	20.9	0.195	4.1
54.0	.002	.0	16.2	.292	6.1
45.7	.002	.0	11.8	.383	8.0
40.4	.011	.2	10.8	.444	9.1
37.4	.022	.5	9.0	.537	11.1
34.0	.028	.6	7.6	.559	11.5
28.8	.078	1.6	6.7	.564	11.6
22.3	.181	3.9			

From this table it is seen that for moisture changes over a wide range near the saturation point there is no change in volume. At about 40 per cent, however, there begins a contraction in volume which continues down to the lowest limit to which the drying was carried. Another curve was obtained by the cathetometer method, the moisture content varying from the saturation point to well below the optimum. At the saturation end of the curve no variation in volume occurred, but at about 35 per cent moisture content a decided contraction began, which continued through the lower moisture contents. These data are given in Table XXI and figure 14.

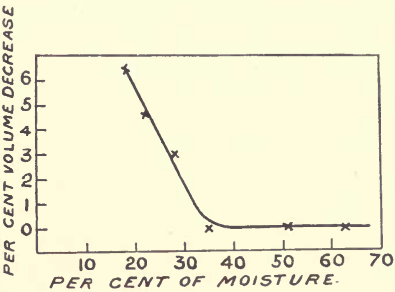

FIG. 14.—Volume-moisture results for Miami black clay loam by the cathetometer method.

TABLE XXI.—*Volume-moisture relations for Miami black clay loam by the cathetometer method.*

Moisture.	Linear decrease.	Volume change.	Moisture.	Linear decrease.	Volume change.
Per cent.	*Centimeter.*	*Per cent.*	*Per cent.*	*Centimeter.*	*Per cent.*
61.2	0.0	0.0	28.2	0.04	3.1
51.8	.0	.0	22.6	.06	4.6
35.0	.0	.0	18.3	.08	6.5

Another set of results on the apparent specific gravity of the different samples is plotted in figure 15, from which it is seen that the results run parallel to the penetration data, as shown in figure 6. Thus, again the volume changes indicate that a change in the physical properties of the soil occurs in the region of the optimum water content.

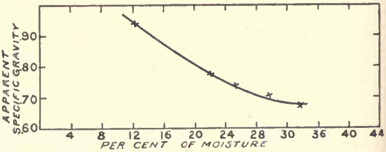

FIG. 15.—Apparent-specific-gravity-moisture results for Miami black clay loam.

Results for Leonardtown loam.

The data and curve for a set of measurements on the volume changes in Leonardtown loam are given in Table XXII and figure 16. This curve does not show a marked change in direction at 15 per cent moisture content, and has been added for the sake of completeness to illustrate what may be expected in volume measurements on a soil of this nature. Numerous attempts to take measurements of the volume changes were made with this soil, from which widely varying results were obtained. A few of the forms of curves resulting from different methods are plotted in figure 17, and show that the behavior of this soil is quite irregular.

TABLE XXII.—*Volume-moisture relations for Leonardtown loam by the micrometer method.*

Moisture.	Linear decrease.	Volume decrease.	Moisture.	Linear decrease.	Volume decrease.
Per cent.	*Centimeter.*	*Per cent.*	*Per cent.*	*Centimeter.*	*Per cent.*
33.0	0.0	0.0	22.6	0.194	6.35
32.4	.029	.96	20.6	.209	6.81
30.0	.097	3.19	17.3	.227	7.32
29.2	.119	3.86	15.9	.230	7.46
27.2	.147	4.79	14.7	.235	7.63
26.2	.166	5.38	12.6	.239	7.76
24.2	.176	5.77	11.7	.241	7.90
23.6	.185	6.03			

The variable conduct of this soil may be attributed to its uncertain plasticity, due to the irregular distribution of clay in the soil. As the soil dries out the particles stick together, and when dry the whole becomes cemented into a very hard and compact mass. This cementing of the particles interferes with whatever tendency the changing moisture condition might have to alter the internal arrangement of the soil.[a]

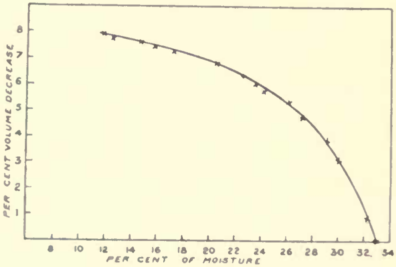

FIG. 16.—Volume-moisture results for Leonardtown loam by the micrometer method.

Upon examination of the curves in figure 2, in which are plotted the penetration results of Puchner, it will be seen that the measurements on clay samples show peculiarities very similar to those encountered in the present work. In the cases in which quartz and humus were in excess the penetration-moisture data all showed maxima in the curves. When kaolin was present in large amounts the penetration values increased steadily as the drying progressed, which action Puchner ascribed to the plastic nature of the material and to the hard, cemented character which the soil assumed on drying out. It is evident from the penetration results for Leonardtown loam that when the sample is worked up into condition at the different moisture contents, the cementing action accompanying drying out is largely prevented.

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[a] The subject of plasticity in clays has been discussed by many writers, and references to a few of the more important treatises are here given: Schlösing, Compt. rend., **74**, 1408 (1872); **78**, 1276 (1874); Jour. de l'agriculture, **9** Iv, 50, 93, 140, 171 (1874) Hilgard, Forsch. auf dem Geb. Agr.-Phys., **2**, 441 (1879); van Bemmelen, Landw. Vers.-Stat., **35**, 69 (1888); Whitney, Bul. No. 4, Weather Bureau, U. S. Dept. Agr. (1892), p. 27; Ries Clays; Their Occurrence, Properties, and Uses. New York, 1906.

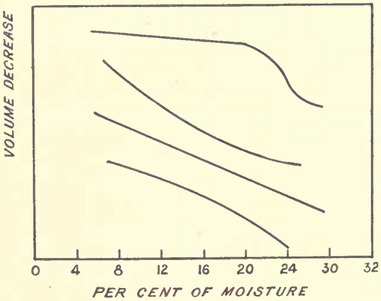

Fig. 17.—Volume-moisture results for Leonardtown loam by the soil column method.

The apparent specific gravity curve shown in figure 18 was plotted from the data contained in Table XXIII. A similar set of data is given in Table XXIV. In all cases there is a well-defined minimum at 15 per cent moisture content.

Table XXIII.—*Relations between penetration, apparent specific gravity, and moisture for Leonardtown loam.*

Moisture, calculated on dry weight of soil.	Weight required for penetration.	Apparent specific gravity.	Moisture, calculated on dry weight of soil.	Weight required for penetration.	Apparent specific gravity.
Per cent.	*Grams.*		*Per cent.*	*Grams.*	
2.8	77	1.07	15.0	43	0.828
6.0	59	.980	15.3	46	.822
10.4	48	.865	17.9	46	.828
12.4	49	.841	20.5	69	.868

Table XXIV.—*Relations between penetration, apparent specific gravity, and moisture for Leonardtown loam.*

Moisture, calculated on dry weight of soil.	Weight required for penetration.	Apparent specific gravity.
Per cent.	*Grams.*	
1.8	50	1.01
5.6	40	.812
11.0	34	.695
14.1	34	.690
17.3	40	.723

Results for muck.

This soil proved to be well suited for measurements on volume change by the soil column method, not only because it retained its form on contraction without developing large cracks, but also because it gave fairly large volume changes. The results of the series of values obtained for volume change with varying amounts of water by the soil column method are given in Table XXV, and shown graphically in figure 19.

TABLE XXV.—*Volume-moisture relations for muck by the soil column method.*

Moisture content.	Linear decrease.	Volume decrease.	Moisture content.	Linear decrease.	Volume decrease.
Per cent.	*Centimeter.*	*Per cent.*	*Per cent.*	*Centimeter.*	*Per cent.*
217.0	0.0	0.0	90.0	0.181	3.8
200.0	.004	.1	83.4	.214	4.46
154.0	.018	.33	67.0	.273	5.31
138.0	.052	1.03	51.1	.372	7.63

From the curve it will be seen that beginning at 217 per cent of moisture, which represents the saturation limit, there is very little decrease in volume over a wide range of moisture content. At 140 per cent of water there is a sharp contraction in the volume which continues down to 45 per cent, the air-dry condition.

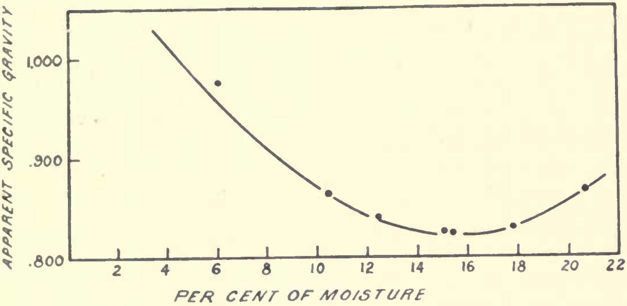

FIG. 18.—Apparent-specific-gravity-moisture results for Leonardtown loam.

A series of check results was obtained by the cathetometer method, and is given in Table XXVI and figure 20. The results are quite like those obtained by the column method, indicating that there is a large change between about 140 per cent of moisture and the air-dry condition. It follows that this soil exhibits the same critical changes in physical properties at the optimum water content as were found in the other soils.

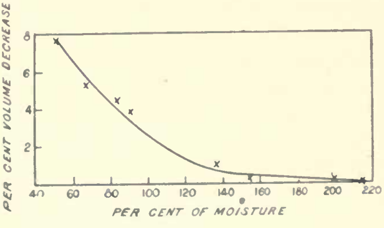

FIG. 19.—Volume-moisture results for Muck by the soil column method.

TABLE XXVI.—*Volume-moisture relations for muck by the cathetometer method.*

Moisture content.	Linear decrease.	Volume decrease.
Per cent.	*Centimeter.*	*Per cent.*
210	0.0	0.0
185	.0	.0
164	.0	.0
120	.01	.76
84	.03	2.4

In figure 8 corresponding results for penetration and apparent specific gravity are given, the abscissas being common to both curves. It will be seen that the two curves are similar, indicating that it is possible to work this soil into the loosest condition at 120 per cent of moisture, at which point the soil is in the best possible agricultural condition. On the addition of water beyond this point the soil soon becomes too wet to be easily worked, as might be predicted from the rapid rise of the penetration curve.

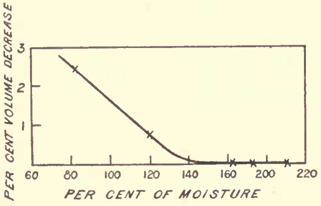

FIG. 20.—Volume - moisture results for Muck by the cathetometer method.

SUCCESSIVE WETTING AND DRYING.

Objects of experiments.

In studying the relation between volume change and moisture content one must consider what constitutes "natural" packing in the soil. It is known that there are large volume changes in soils under field conditions whenever the soil is dried or wetted. These volume changes render it highly improbable that the soil will stay in any condition of packing imposed by an external agency. It is a matter of common observation that when a soil is put into a loose condition by cultivation or other means and subsequently left undisturbed it will settle back in time nearly to its original volume. The relation between the change in volume due to settling and the change in volume due to a variation in moisture content was therefore investigated.

Experimental methods.

The methods of measuring the volume changes were the same as in the volume work described above. When the soil had gone through the process of drying out once it was wetted by capillary rise without in any other way disturbing it. A complete record of the volume measurements was obtained while the soil was drying out; the total change in volume due to wetting was observed without obtaining measurements for the intermediate moisture contents. This cycle could be repeated any number of times, and the variation in soil volume due to continued wetting and drying could be readily followed.

Results for Miami black clay loam.

The results of a set of measurements by the soil-column method for Miami black clay loam in which the original sample was in fairly loose condition are given in Table XXVII. For each cycle the volume decrease has been given in cubic centimeters and in per cent. In the last column is given the total volume decrease referred to the original volume. The separate curves are referred to the same standard for comparison, i. e., the original volume of the sample.

TABLE XXVII.—*Volume changes for the continued wetting and drying of a loose sample of Miami black loam. (Soil column method.)*

Cycle.	Moisture content.	Length of column.	Changes during separate dryings.		Total changes from original condition.	
			Linear decrease.	Volume decrease.	Linear decrease.	Volume decrease.
	Per cent.	*Centimeters.*	*Centimeter.*	*Cubic centimeters.*	*Centimeters.*	*Cubic centimeters.*
1	53.2	13.989	0.0	0.0	0.0	0.0
	41.1	13.989	.011	.2	.011	.2
	38.5	13.936	.064	1.3	.064	1.3
	25.2	13.904	.196	4.1	.196	4.1
	19.2	13.545	.455	9.3	.455	9.3
	9.5	13.366	.634	12.9	.634	12.9
	5.7	13.316	.684	14.0	.684	14.0
2	59.0	13.536	.0	.0	.464	9.8
	54.0	13.534	.002	.0	.466	9.8
	45.7	13.534	.002	.0	.466	9.8
	40.4	13.525	.011	.2	.475	10.0
	37.4	13.514	.022	.5	.486	10.3
	34.0	13.508	.028	.6	.492	10.4
	28.8	13.458	.078	1.6	.542	11.4
	22.3	13.455	.181	3.9	.645	13.7
	20.9	13.341	.195	4.1	.659	13.9
	16.2	13.244	.292	6.1	.756	15.9
	11.8	13.153	.383	8.0	.847	17.8
	10.8	13.092	.444	9.1	.908	18.9
	9.0	12.999	.537	11.1	1.001	20.9
	7.6	12.977	.559	11.5	1.023	21.3
	6.7	12.972	.564	11.6	1.028	21.4
3	58.3	13.469	0.0	0.0	0.531	10.5
	55.6	13.428	.041	.9	.572	11.4
	51.4	13.407	.062	1.3	.593	11.8
	37.2	13.373	.096	2.1	.627	12.6
	31.8	13.318	.151	3.2	.684	13.7
	22.1	13.195	.274	5.8	.805	16.3
	19.8	13.131	.338	7.2	.869	17.7
	15.5	13.000	.469	9.7	1.000	20.2
	12.3	12.858	.611	12.5	1.142	23.0
	9.4	12.809	.660	13.5	1.191	24.0
	7.8	12.793	.676	13.8	1.207	24.3
4	59.5	13.282	.0	.0	.718	14.6
	54.5	13.271	− .011	− .08	.729	14.5
	40.0	13.153	+ .029	+ .6	.747	15.2
	32.4	13.114	.068	1.4	.786	16.0
	21.0	13.107	.175	3.7	.893	18.3
	19.3	13.092	.190	4.0	.908	18.6
	14.9	13.027	.255	5.3	.973	19.9
5	56.0	13.218	.0	.0	.782	15.9
	34.8	13.151	.067	1.4	.859	17.3
	2.9	13.071	.147	3.1	.929	19.0

From the data for total volume change it can be seen that there is a decrease in volume on drying out the wet sample. When the dry soil is wet again, there is an expansion, which is not, however, as large as the previous contraction, so that the total effect for the cycle has been to reduce the volume of the sample. The effect of continually wetting and drying a loose sample of soil is better seen from the curves in figure 21, which have been plotted from the data given in the above table.

The volume decrease for the loose soil in drying from a saturated to an air-dry condition was about 14 per cent of the original. This change is represented by curve 1. On again wetting the dry soil, it still showed a volume of 10 per cent less than the original. If on drying out the second time the moisture content had been reduced as low as it was in the case of curve 1, the volume change would have been about 12 per cent. This can be seen by exterpolating curve 2 to a 5 per cent moisture content.

The volume change from the original condition is about 23 per cent; hence at the end of this drying the soil occupies 77 per cent of its original volume. Likewise when this dry sample was wetted again, the expansion was less than the previous contraction, so that at the end of the second cycle the sample was packed still more. The difference, however, between states 3 and 2 is much less than between 2 and 1. The volume occupied by the soil after the third wetting decreased 13.8 per cent on drying out, which indicates that, although the sample is packed more tightly, the contraction in passing from a saturated to an air-dry condition remains about the same. The results for the fourth and fifth dryings are represented by curves 4 and 5, and in general indicate that the changes due to successive wettings and dryings are more nearly identical and that the sample is approaching a condition of "natural" packing.

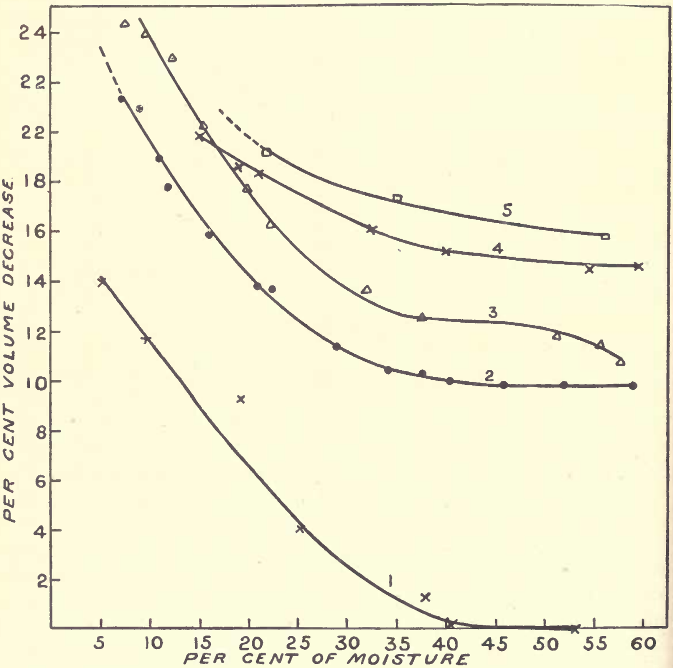

FIG. 21.—Volume changes with successive wetting and drying of loosely packed Miami black clay loam.

By the time curves 4 and 5 were obtained the soil column was in rather poor condition, owing to the fact that the cracks which formed on drying were not repaired in the subsequent wetting, so that the soil column developed points of weakness which interfered with the measurements of the total volume changes. For a continued series of this kind the soil column method would not prove so satisfactory as a method in which the sample is contained in a dish and the height of the soil surface measured. The former method has, however, the distinct advantage of being rapid, since the surface exposed per gram of soil is relatively very much greater than if the sample were contained in a cup. It is probable that the first three curves are more reliable than those obtained when the soil column was weakened by cracks.

These measurements on the continuous contraction of a loose sample of Miami black clay loam lead to the following conclusions:

(1) On drying and wetting a loose sample of soil there is a marked hysteresis effect in the volume changes, resulting in a total contraction in volume for a moisture-change cycle.

(2) On successive wettings and dryings this hysteresis becomes less and less. When it disappears altogether, the expansion on wetting will be equal to the contraction on drying and a condition will have been attained which may be designated a "natural" packing of the soil.

(3) Curves 1, 2, and 3 show that within limits the contraction in drying from a saturated to an air-dry condition is not greatly dependent on the packing.

Results for Muck.

A sample of Muck in a loose condition was found to give similar results for successive wettings and dryings. The contraction on drying out the sample the first time was 29.2 per cent of the original volume. On wetting it increased, however, only 7 per cent; as the result, therefore, of one cycle the volume was 22.2 per cent less than originally. On drying out the second time the volume decrease was 7.6 per cent, which made a total volume decrease of 29.8 per cent.

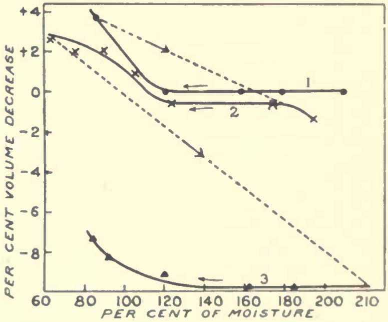

Fig. 22.—Volume changes with successive wetting and drying of closely packed Muck.

That the condition of natural packing in a soil does not represent the closest possible packing is evident from observations made on the successive wetting and drying of a very tightly packed sample of Muck. The soil, in a moderately moist condition, was closely packed into a cup and the change in volume with moisture content was followed by the cathetometer method. The results stated in Table XXVIII are expressed in the same manner as in Table XXVII, except that when the volume of the sample becomes greater than in the original condition the total per cent decrease in volume is assigned a negative value. The original saturated condition is taken as zero on the percentage volume change scale, and increases and decreases in volume are figured down and up respectively from this point. The results are more easily appreciated from the corresponding curves in figure 22. The curves have been numbered in the order of the successive dryings. On drying out the original sample the usual volume contraction is noted. The direction of the change (not the actual path) on wetting is indicated by the arrows on the dotted lines. In this case the expansion on wetting was greater than the previous contraction, and at the end of cycle 2 the sample is in looser condition and occupies a greater volume than at the end of cycle 1. Curve 2 again shows a contraction on drying and a much greater expansion on wetting. Curve 3 also shows the usual contraction on drying.

TABLE XXVIII.—*Volume changes for the continued wetting and drying of a closely packed sample of Muck (cathetometer method).*

Cycle.	Moisture content.	Linear decrease.	Volume decrease.	Difference in volume.	Total volume decrease.
	Per cent.	*Centimeter.*	*Per cent.*	*Per cent.*	*Per cent.*
1....	205.0	0.0	0.0	0.0	0.0
	179.0	.0	.0	.0	.0
	158.0	.0	.0	.0	.0
	120.0	.0	.0	.0	.0
	86.0	.05	3.98	.0	3.98
2....	195.0	.0	.0	−1.32	−1.32
	175.0	.01	.76	.0	− .56
	123.0	.01	.76	.0	− .56
	105.0	.03	2.39	.0	+1.05
	92.5	.04	3.13	.0	+2.08
	75.0	.04	3.13	.0	+2.08
	64.0	.05	3.98	.0	+2.66
3....	210.0	.0	.0	−9.8	−9.80
	185.0	.0	.0	.0	−9.80
	164.0	.0	.0	.0	−9.80
	120.0	.01	.76	.0	−9.04
	92.0	.02	1.58	.0	−8.22
	84.0	.03	2.39	.0	−7.41

In comparing this with the curves representing the continuous changes in a loose sample (fig. 25) the effect of continued wetting and drying is seen to be in an opposite direction. It is possible therefore to pack a soil so tightly that on continuous moisture changes the volume will increase. This hysteresis effect will cease when the expansion due to complete wetting just equals the contraction due to drying out to the air-dry condition, and the soil will then be in the state of natural packing. It has been suggested that within narrow imits the change in volume on contraction was not greatly dependent on the packing. If this were not the case the influence of packing would have to be considered in measurements, such as were made by Wollny and others, on the "total" volume change due to wetting and drying. It has been made clear that unless the condition of natural packing is realized the volume decrease in drying will not be the same as the increase in the subsequent wetting. That the volume changes obtained by previous investigators (see Tables XIV and XV) on wetting a soil were different from those obtained for the same soil on drying was no doubt due to the fact that the samples were not in the condition of natural packing and that the hysteresis effects described above were encountered.

RATE OF EVAPORATION.

RELATION OF RATE OF EVAPORATION TO MOISTURE CONTENT.

Experimental methods.

Since vapor pressure, and hence rate of evaporation, varies with temperature, reliable results could be obtained only when the measurements were made at constant temperature. A large air thermostat was made for this purpose. In order to cut down radiation the walls were built double. The heating was done by electric lamps controlled by the Geer[a] form of electric thermo-regulator. The air was thoroughly stirred by means of a fan, driven from the outside by a motor. By means of this device the temperature could be maintained constant within 0.1° C. In order that the humidity might remain constant during evaporation the samples were put in desiccators over a relatively large surface of 95 per cent sulphuric acid, which maintained a partial vapor pressure of 0.1 millimeter mercury at 25° C., the temperature of the thermostat.

Thus by regulating the temperature and consequently the vapor pressure the conditions for evaporation were controlled satisfactorily.[b]

The method consisted of wetting to its saturation point an amount of soil equivalent to 20 grams of dry material. The weight of the bottle and soil was determined initially and at frequent intervals during the process of drying out in the desiccator. From the loss in weight and the time between successive weighings the rate of evaporation was calculated. From the observed weight of the soil and bottle and the dry weight equivalent of the soil, the moisture content at the time of weighing was calculated. The calculated rate of evaporation was based on the mean water content prevailing over the time in which the loss was occurring, i. e., the mean of the moisture contents calculated from two successive weights.

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[a] Jour. Phys. Chem., 6, 85 (1902).

[b] Under these conditions the rate of evaporation from a dish of water should of course be constant. This was tried experimentally with satisfactory results.

Results for Podunk fine sandy loam.

A series of measurements on the rate of evaporation for Podunk fine sandy loam is given in Table XXIX, and is represented graphically in figure 23.

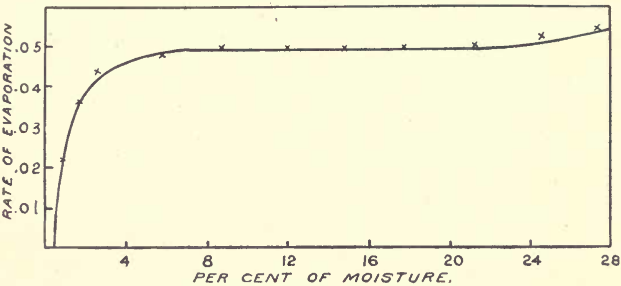

Fig. 23.—Rate-of-evaporation-moisture results for Podunk fine sandy loam.

Table XXIX.—*Rate of evaporation from Podunk fine sandy loam over 95 per cent sulphuric acid at 25° C.*

Mean moisture content.	Time interval.	Loss.	Loss per hour.	Mean moisture content.	Time interval.	Loss.	Loss per hour.
Per cent.	*Hours.*	*Gram.*	*Gram.*	*Per cent.*	*Hours.*	*Gram.*	*Gram.*
27.4	19.5	1.0450	0.0536	8.7	14.5	0.7140	0.0492
24.2	4.5	.2362	.0525	5.8	9.9	.4712	.0476
21.3	18.7	.9210	.0493	2.4	4.0	.1732	.0433
17.8	9.3	.4595	.0494	1.7	2.0	.0719	.0359
14.8	15.3	.7495	.0490	.9	11.0	.2445	.0222
12.0	9.9	.4854	.0490	.3	2.0	.0097	.0049

The measurements on the rate of evaporation were begun when the soil held 28 per cent of water. The first evaporation was probably from the surface alone, so at first there is a small decrease in the rate as the water begins to evaporate from the pore spaces. Beginning at 22 per cent of water and extending over a wide range the rate of evaporation remains quite constant. At about 6 or 7 per cent a change takes place, for the rate decreases and continues to fall rapidly as the percentage of moisture decreases. Again, there is an obvious change in the physical properties of the soil at the optimum water content.

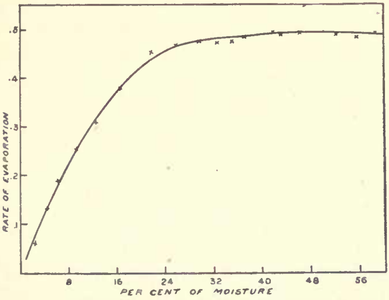

Fig. 24.—Rate-of-evaporation-moisture results for Miami black clay loam.

Results for Miami black clay loam.

On account of the high water content at the optimum in this soil the rate of evaporation method was exceptionally well suited to furnish a comparison of the soil condition at different water contents. The optimum for Podunk fine sandy loam lies so low that the change in the curve for the rate of evaporation might be supposed to be due to the relatively dry condition alone. In the present case the optimum lies about 30 per cent above the air-dry condition, so that changes in the character of the curve for rate of evaporation will be more significant. The data for this curve were obtained in the same way as for Podunk fine sandy loam. The data and the graphical representation are given in Table XXX and figure 24.

The evaporation curve which was started near 60 per cent is horizontal for about 20 per cent decrease in moisture content, showing a uniform rate above the optimum. At about 40 per cent, however, it gradually changes direction, the rate of evaporation falling.

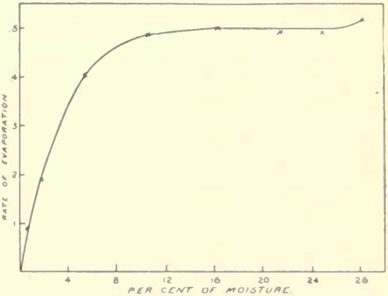

Fig. 25.—Rate-of-evaporation-moisture results for Leonardtown loam.

Table XXX.—*Rate of evaporation from Miami black clay loam over 95 per cent sulphuric acid at 25° C.*

Mean moisture content.	Time interval.	Loss.	Loss per hour.	Mean moisture content.	Time interval.	Loss.	Loss per hour.
Per cent.	*Hours.*	*Gram.*	*Gram.*	*Per cent.*	*Hours.*	*Gram.*	*Gram.*
58.5	16.7	0.8198	0.0491	29.7	7.0	0.3321	0.0174
55.4	9.3	.4174	.0481	26.9	17.0	.7964	.0468
52.4	15.17	.7422	.0489	22.1	24.0	1.0879	.0453
49.4	9.9	.4802	.0485	17.1	24.0	.9109	.0379
46.4	14.5	.7155	.0493	12.9	26.25	.8108	.0309
43.4	9.9	.4808	.0486	9.5	22.25	.5716	.0257
41.0	11.0	.5427	.0492	6.7	24.5	.4694	.0192
37.5	11.0	.5411	.0483	5.1	22.75	.3056	.0134
35.4	6.5	.3099	.0477	3.7	23.75	.2136	.0090
32.6	17.5	.8295	.0474	2.7	24.25	.1470	.0061

For Miami black clay loam the studies in penetration, apparent specific gravity, and rate of evaporation all indicate that the critical moisture content which determines the physical properties of this soil lies between 35 and 40 per cent, which also is the optimum water content of the soil.

Results for Leonardtown loam.

The measurements of rate of evaporation from Leonardtown loam are given in Table XXXI and figure 25.

It has been shown that for this type of soil the volume relations at the optimum water content do not permit of very satisfactory conclusions. However, the penetration and evaporation measurements show critical changes at about 15 per cent of water, the optimum water content of the soil.

TABLE XXXI.—*Rate of evaporation from Leonardtown loam over 95 per cent sulphuric acid at 25° C.*

Mean moisture content.	Time interval.	Loss.	Loss per hour.	Mean moisture content.	Time interval.	Loss.	Loss per hour.
Per cent.	*Hours.*	*Gram.*	*Gram.*	*Per cent.*	*Hours.*	*Gram.*	*Gram.*
28.2	19.0	0.9770	0.0517	10.7	24.5	1.1963	0.0488
24.9	7.25	.3555	.0490	5.5	22.75	.9193	.0404
21.6	19.25	.9538	.0495	2.0	24.25	.4560	.0188
16.4	22.0	1.0962	.0498	.7	24.16	.0904	.0037

Results for muck.

The results for this soil are given in Table XXXII, and have been plotted in figure 26. When the soil in a very wet condition was put over sulphuric acid in a desiccator there was at first a rapid drop in the rate of evaporation corresponding to the decrease as in the previous cases studied. The curves, however, indicate that for a wide change in moisture content it exhibits very little change in the rate of evaporation. At about 120 per cent there is a rapid decrease in the rate of evaporation, indicating that the critical moisture content has been reached. This decrease continues down to 30 per cent, at which point measurements were discontinued.

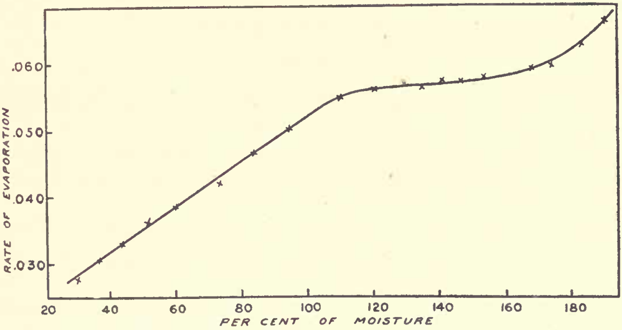

FIG. 26.—Rate-of-evaporation-moisture results for Muck.

TABLE XXXII.—*Rate of evaporation from muck over 95 per cent sulphuric acid at 25° C.*

Mean moisture content.	Time interval.	Loss.	Loss per hour.	Mean moisture content.	Time interval.	Loss.	Loss per hour.
Per cent.	*Hours.*	*Gram.*	*Gram.*	*Per cent.*	*Hours.*	*Grams.*	*Gram.*
190	9.5	0.6362	0.0669	110	24.0	1.3233	0.0551
183	15.2	.9590	.0632	95	24.0	1.2120	.0505
174	9.85	.5905	.0600	84	26.3	1.2332	.0469
168	14.5	.8639	.0596	74	22.1	.9329	.0423
154	10.0	.5813	.0581	60	24.3	.9388	.0387
147	13.0	.7474	.0575	52	23.0	.8352	.0363
141	6.5	.3744	.0576	44	24.0	.7958	.0331
135	17.5	.9893	.0566	37	24.0	.7372	.0307
121	17.0	.9591	.0564	30	24.5	.6851	.0279

MOISTURE DISTRIBUTION.

MOISTURE FILMS.

When to a dry soil a very small amount of water is added by putting the sample in an atmosphere saturated with vapor, there will be a direct condensation on the soil grains, and water will be held partly or entirely in thin films on the surface of the soil particles. Owing to an attraction between the particles and the water at the surface, this absorbed moisture is held with very great force, and the wetting of the soil grains is accompanied by an energy change of considerable magnitude. On wetting a mass of dry soil the formation of this film in the manner stated is accompanied by another effect due to the contact of soil grains. The films merge, so that a number of soil grains may be considered as being covered by one continuous film, and pulled together at the points of contact by the tension of the connecting film. Considering for the moment the formation of the films around the grains, it is evident that as more water is added to the soil and the films get thicker a point will be reached where the surface attraction of the soil particle is no longer strong enough to retain more water, since the surface force decreases rapidly as the distance from the surface increases.[a]

Before this point is reached, however, the thickness of the water films at the point of contact between the grains has been increasing owing to the film tension at the points of high curvature in the angles between the grains.[b] The thin, wedge-shaped angles between the grains will act then as capillary spaces and help to hold water. Since the surface films and capillary films merge, it is impossible to distinguish between them. The forces exerted by these films determine the changes in the internal arrangement of the soil particles and the physical characteristics of the soil.

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[a] Bakker, Zeit. phys. Chem., **56**, 95 (1906).
[b] Briggs, Bul. No. 10, Bureau of Soils, U. S. Dept. Agr. (1897).

EFFECT OF MOISTURE DISTRIBUTION ON VOLUME CHANGES.

When a soil is saturated with water the pore spaces are filled. Assuming that these soil capillary tubes are continuous and of uniform diameter, the capillary force holding the water is equal to the pull in an ordinary capillary tube of a similar size. In comparison with the capillary spaces occurring at the contact of the soil grains, these tubes are large, so that the capillary force exerted by them is relatively small. Since the water in the large spaces is not held by great force, it will be the first to evaporate and will have but little effect in changing the arrangement of the grains. As evaporation proceeds a point will be reached where the water begins to evaporate from the fine capillary spaces, which include the angles between the soil grains. At this point the forces of film tension become more noticeable. As the water held between the soil grains diminishes and retreats farther and farther into the angles, the surface film stretches, increasing the film tension and pulling the soil grains inclosed by it still closer together, thus producing a contraction in the volume occupied by the soil. The point where the effective film forces are just sufficient to cause changes in the internal soil arrangement will be designated the "critical moisture content." As evaporation continues still further the surface films around the grains and the capillary wedges held between the grains become thinner. The surface film forces continue to increase; hence the volume should steadily decrease until the soil reaches an air-dry condition.

It is evident from the data given for the volume changes in Podunk fine sandy loam that the above consideration is substantiated by experimental facts, and even more strongly by the volume changes observed with the other soils. Take, for example, Podunk fine sandy loam with about 14 per cent of water. At this point the large pore spaces contain considerable water, and as the soil dries out this water will be the first to disappear. Since the large capillary tubes constitute a relatively large part of the soil space available for water, they will hold a considerable percentage of the water when the soil is saturated. This will be particularly true in this soil, a sand, where the single intergranular spaces are large, owing to the size of the soil particles. The withdrawal of water from the larger pore spaces will therefore cause a large decrease in the moisture content of the soil. When the moisture content of the soil is about 6 per cent, the critical water content is reached and a change in volume begins.

It will be remembered that for volume changes in Podunk fine sandy loam a large volume contraction occurred between 33 and 18 per cent of water, between which limits the soil is too wet to ascribe the variation to the tension of the surface films. As the measurements were made on fairly loose samples of soil, it is quite possible that this volume change was caused simply by a gradual settling of the wet soil particles. When wet beyond a certain point a sand becomes incoherent. The soil aggregates seem to break down and the grains slip easily over one another, the excess of water acting as a lubricant and reducing the friction between the grains. It is possible that the volume changes occurring near the saturation point may also, in part, be due to a tendency of the free water to buoy up the soil grains and in this way decrease the packing of the grains by lowering the effective specific gravity of the individual grains. As the wet soil dries out, this tendency decreases and vanishes at a content of water a little below the saturation point.

The larger volume changes due to addition of water in clay soils is sometimes attributed to the presence of large amounts of colloidal material, which is supposed to imbibe the water and swell like starch grains. This view can easily be brought into agreement with the above theory of volume change. The question of absorption in a cell has been quite fully considered by Kauffler[a] and it has been shown by Patten[b] that absorption with imbibition can be considered as a special case under absorption. For our purpose, therefore, it makes no difference whether the volume change is due to action on the exterior surface of the particles or to imbibition accompanied by an increase in size of the particles. In the case of a peat soil, for example, it seems entirely reasonable that on account of the nature of the material a large change in volume is due to imbibition and swelling of the cells. There is no reason why a similar view should not be held for clay, although here it is quite possible to explain the phenomena without recourse to this idea. The volume changes in clay are very much greater than in sand. On account of the large difference in soil surface in a similar volume of the two classes, we would also expect the capillary and film effects in clay to be very much greater. The proportion of the relative areas exposed by equal volumes of very fine sand and of clay may be as great as 1 to 300, a difference which is quite sufficient to explain the large differences in volume changes in the two soils, on the basis of surface absorption and surface tension.

EFFECT OF MOISTURE DISTRIBUTION ON PENETRATION.

Having shown that volume changes in soils can be explained on the basis of the forces exerted by the capillary and surface films around the grains, and that the critical water content for volume-change and that for penetration are identical, it remains to be seen how the above considerations regarding the distribution of water in the soil explain the phenomena observed in the penetration experiments.

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[a] Zeit. phys. Chem., **43**, 686 (1903).

[b] Trans. Am. Electrochem. Soc., 11 (1907).

Consider first the case of penetration under conditions of loose structure. The variations in the penetrability of the soil were attributed to the ability of the soil grains to arrange themselves into aggregates. In a dry soil the cohesion between the grains is that of one dry, solid body for another, and is readily seen to be small. The particles are thus quite free to move each other and tend to settle down into a compact condition. When a small amount of water is added to the soil, it gathers over the surface as films and settles into the angles between the soil grains. The cohesion of the soil particles increases and the action of surface tension promotes the formation of floccules and increases the possibility of building up the soil into a loose structure. As more water is added the thickness of the films and the amount of water held in the angles between the grains increase, the cohesion increases, and the soil responds better to cultivation. This effect reaches a maximum when the amount of water that can be held in this way reaches a maximum, and will be indicated by the fact that a minimum amount of force will be necessary to penetrate the soil sample. Since the loosely arranged soil grains in this condition occupy the smallest possible percentage of the total volume of the soil, the remainder of volume being taken up by air, the resistance to the introduction of a penetrating tool is a minimum at this point.

The further addition of water beyond the critical moisture content begins to fill up the larger pore spaces and to flood the soil. The soil aggregates begin to break down, thereby increasing the force necessary for penetration. This is shown by a gradual rise in the penetration curve beyond the minimum. Parallel results are, of course, indicated on the apparent specific gravity curves. The variations in penetration with moisture content is therefore related to differences in the distribution of water in the soil.

This same theory of soil moisture distribution accounts for the penetration results obtained by the Puchner method, where the critical water content for penetration was indicated by a maximum. As dry soil was packed into the containing vessel, the sample can be considered to represent a "single grain structure." The wetting of this dry sample must have been accompanied by an increase in volume, which caused an upward movement of the soil surface and a horizontal thrust upon the sides of the vessel. This acted as a packing force to the already close arrangement. The wetting of the soil also caused an increase in cohesion, as has been pointed out above. If the penetration measurements, therefore, had been made first on the dry sample and then on the sample corresponding to the maximum cohesion, there should be noted an increase in the penetration value. When a soil is saturated with water, the flotation effect tends to susend the particles and decrease the packing. The excess of water, vhich renders the soil incoherent, acts as a lubricant, and increases he ease with which the soil grains slide over each other. At saturaion this effect is greatest, so that the resistance to penetration is east. As the percentage of water decreases, this effect decreases, and he penetration values rise as shown by the curves. When the water lisappears from the larger pore spaces, the critical moisture content ınd the point of maximum cohesion is reached, at which point the acking effect due to wetting the soil in a confined space is still in force so that the penetration value is high. As the amount of water further decreases there is a decrease in volume due to drying as ılready shown and a corresponding diminution of this horizontal thrust on the walls of the dish which causes a decrease in the penetration value. Therefore for a soil sample treated in this way the maximum force required for penetration is necessary at the critical moisture content. In the case of Podunk fine sandy loam the occurrence of the critical point in the penetration-moisture relations in both methods of measurement at about 6 per cent of moisture is not a mere coincidence, but is due to the same fundamental forces exerted by a certain quantity of soil moisture in its distribution upon the soil particles.

The change in the physical properties of a soil may be referred to one particular percentage of water only in case the distribution of the water in the soil is entirely uniform, which condition of course does not occur ordinarily. The distribution of water is affected in some measure by the size of the grains, irregularities in packing, gravity, and other variables which can not be controlled. The condition which has been described as influencing the internal arrangement of the soil grains can not then be correctly ascribed to a single point in the moisture variation, but must be considered as operating over a more or less narrow range of moisture content and subject to slight variation from sample to sample of one soil. Also, the measurement of this range may give slightly different results, depending on the method used. From a theoretical point of view the variation in range due to differences in the conditions prevailing does not detract from the value of the results or of the conclusions reached, since the cause of this variation is clear.

EFFECT OF MOISTURE DISTRIBUTION ON RATE OF EVAPORATION.

A further confirmation of the view that the content of soil moisture determines the physical properties of the soil is furnished by the investigation on the rate of evaporation of soil water from soils containing different percentages of water. It has been pointed out that a great difference must exist between the forces with which the water is held in the larger pore spaces and in the capillary angles between the grains. From this the conclusion follows that there must be a corresponding difference in the rate of evaporation.

As the water evaporates out of the larger pore spaces, the rate of evaporation will be determined by diffusion and by the forces of capillarity. Since a considerable quantity of the total soil water is held in the larger pore spaces and since the capillary pull in these spaces is not great in comparison with the forces exerted in the fine angles between the grains, the influence of capillarity upon evaporation from the large spaces will be relatively small. In relation to the rate of evaporation much of the intergranular space can be considered to be of the same order of magnitude, for which reason the rate of evaporation over a considerable range will not decrease very rapidly while the soil is drying out. As the evaporation continues the water held in these pores will disappear, and the soil water will be distributed almost entirely in the fine capillary angles between the soil grains and on the grains as films, where the greater capillarity holds it more strongly. Below this critical moisture content there will be a gradual falling off in the rate of evaporation, due to the increasing attractions between the water and the soil, causing a lowering of the vapor pressure of the absorbed films. Where the thickness of the film is such that the surface attraction just begins to cause a lowering in the vapor pressure of the film, the equilibrium point between the soil moisture and a saturated atmosphere of water vapor is reached, and in such an atmosphere no further evaporation of water from the soil grains takes place. In the open air, however, we are not dealing usually with a saturated atmosphere, and so evaporation will continue from the soil, but under constantly decreasing vapor pressure of the absorbed water, which in turn will cause a corresponding decrease in the rate of evaporation. When the vapor pressure of the soil films corresponds to the partial pressure of the moisture in the atmosphere, evaporation will cease, equilibrium having been reached between the vapor in the air and the film water.

Below the critical moisture content there will be a decrease in the rate of evaporation due, first, to slower diffusion of the water vapor from the finer capillary spaces, and, second, to an increase in the film tension accompanied by a decrease in the vapor pressure of the film water. These two effects merge gradually one into another, so that a smooth curve showing the decrease in evaporation is the result, the rapid decrease in evaporation beginning when the water in the larger pore spaces has nearly disappeared.

CRITICAL MOISTURE CONTENT AND MOISTURE EQUIVALENT.

That there is a connection between the critical moisture content and the distribution of soil moisture follows, also, from recent work done in this Bureau.[a] By means of a centrifugal machine a wet soil sample was subjected to a force about 3,000 times that of gravity, which tended to throw the water from the soil. Even when subjected to such a force it was impossible to reduce the soil sample to an approximately dry condition; in fact, the resulting soil samples contained enough moisture to correspond to good field condition. It is evident from this that part of the water is held in the soil by very strong forces. The only moisture removed from the soil was that held in the larger pore spaces. When the moisture content of the soil is reduced to the point where the water is held in the form of films and as capillary water between the soil grains, it is retained more tenaciously. It was also pointed out that the amount of water removed from the soil is not directly proportional to the centrifugal force used; that is, the soil can be reduced from very wet to a medium condition by a relatively small force. If at this point the speed be doubled, which means that the centrifugal force will be quadrupled, the further reduction of moisture content is comparatively small. This is in agreement with the conclusions reached from the present studies on the rate of evaporation from soils. Instead of measuring the retentiveness of the soil in terms of centrifugal force, here the effect of such a retentiveness on the rate of evaporation has been measured. When the soil moisture is held in the larger pore spaces, the rate of evaporation is fairly constant and not very much less than would be obtained under similar conditions from a free water surface. In other words, the retentiveness of the soil is not very great as indicated by the rate at which that part of the soil moisture evaporates. However, when the critical moisture content is reached, the rate of evaporation immediately begins to decrease, indicating that the soil water is held by greater forces in the finer capillary spaces. As the water surfaces retreat farther into the angles between the grains and the films on the grains become thinner, the forces holding the soil moisture in place increase; this in turn produces a decrease in the rate of evaporation. The results obtained by the centrifugal method agree with the rate of evaporation results, indicating the point at which the larger soil forces come into play. To compare these two methods of studying the distribution of soil moisture one may use the measurements of Briggs and McLane on Norfolk fine sandy loam and the measurements above recorded on Podunk fine sandy loam. The Norfolk fine sandy loam very closely resembles the Podunk fine sandy loam in its physical characteristics. This similarity is shown in part by the comparison of the mechanical analyses of the two soils given in Table XXXII.

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[a] Briggs and McLane, Bul. No. 45, Bureau of Soils, U. S. Dept. Agr. (1907).

TABLE XXXIII.—*Mechanical analyses of Podunk fine sandy loam and of Norfolk fine sandy loam.*

Soil.	Fine gravel, 1 to 2 millimeters.	Coarse sand, 1 to 0.5 millimeter.	Medium sand, 0.5 to 0.25 millimeter.	Fine sand, 0.25 to 0.1 millimeter.	Very fine sand, 0.1 to 0.05 millimeter.	Silt, 0.05 to 0.005 millimeter.	Clay, 0.005 to 0.0 millimeter.
Norfolk fine sandy loam.......	0	0.5	4.8	54.6	13.4	18.1	8.5
Podunk fine sandy loam.......	0	0	1.0	47.6	30.4	18.8	2.2

From this comparison it is seen that both soils contain a larger percentage of fine sand than of any other separate and that the quantities in the two soils are comparable. The Podunk soil contains somewhat more very fine sand than the Norfolk soil. The amount of silt is the same in both cases, but the amount of clay in the Podunk fine sandy loam is less than in the Norfolk fine sandy loam. By means of the centrifugal method the "moisture equivalent" was found to be 6.5 per cent of moisture. The critical condition of soil moisture for Podunk fine sandy loam, determined by the rate of evaporation method, was found to be 6 per cent, which is in agreement with the critical moisture value for this same soil as determined from the penetration and volume-change studies. The value obtained from the similar Norfolk fine sandy loam by the centrifugal method is just a little higher, which may easily be attributed to the higher clay content of that soil, since we know that the clay in a soil exerts a large influence on its water-holding power. As no determinations are available for the "moisture equivalent" of Muck or of the Miami black clay loam, there is no basis for comparison of these results. It is possible, however, to compare the sample of Leonardtown loam used in our investigations with a Hagerstown silt loam and a Clarksville silt loam, studied in the centrifugal work of Briggs and McLane.

A comparison of the mechanical composition of these three soils is given in Table XXXIV.

TABLE XXXIV.—*Mechanical analyses of Leonardtown loam, of Clarksville silt loam, and of Hagerstown silt loam.*

Soil.	Organic matter.	Gravel, 2 to 1 millimeters.	Coarse sand, 1 to 0.5 millimeter.	Medium sand, 0.5 to 0.25 millimeter.	Fine sand, 0.25 to 0.1 millimeter.	Very fine sand, 0.1 to 0.05 millimeter.	Silt, 0.05 to 0.005 millimeter.	Clay, 0.005 to 0.0 millimeter.
Leonardtown loam ...	....	0.1	1.2	0.9	3.1	6.4	70.9	16.7
Clarksville silt loam ..	1.2	1.2	1.4	.9	2.0	5.6	73.2	14.8
Hagerstown silt loam.	1.0	.3	.6	1.5	9.1	10.5	60.3	17.4

Clarksville silt loam more closely resembles the Leonardtown loam than does the Hagerstown silt loam. In all of these soils silt is in excess, varying from 60.3 to 73.2 per cent for the three soils. As regards this point, the Leonardtown and the Clarksville soils are closely comparable. The clay contents are about the same, being slightly higher in the Hagerstown silt loam. The "critical moisture content" was found to be about 15 per cent for the Leonardtown loam. The "moisture equivalent," as determined by the centrifugal method, for the Clarksville soil was 15.1 and for the Hagerstown sample 16.5. From the close similarity in the mechanical composition and in the moisture values given, it would appear that the *critical moisture content* corresponds to the *moisture equivalent* as determined by the centrifugal method, as well as to the optimum water content, as determined by plant growth and cultural practices.

OPTIMUM WATER CONTENT AS REGARDS PLANT GROWTH.

The usual definition of optimum water content is that amount of water in the soil which is best suited to plant growth. But no emphasis has been placed on this during the course of the previous discussion, where it has been spoken of more often as the amount of water determining the best physical condition of the soil. It can be shown that the amount of water determining the best physical condition of the soil is generally the amount of water most favorable to plant growth. In this connection some evidence is given by Heinrich,[a] who determined the amount of water present in the soil when wilting of plants begins. In the six soils used determinations were made of the point of saturation, of the moisture content at which plants wilt, and also of the hygroscopic water content. This last was done by spreading the soil on a watch glass and exposing it for a week to an atmosphere saturated with water vapor. The results of this investigation are given in Table XXXV.

TABLE XXXV.—*Relation between hygroscopic moisture content and moisture content at which plants begin to wilt, according to Heinrich.*

Soil.	Water content at saturation.	Hygroscopic water content.	Moisture content at which plants begin to wilt.
	Per cent.	*Per cent.*	*Per cent.*
Coarse sand	26.5	0.42	1.5
Medium fertile garden soil	43.9	1.68	4.6
Infertile sandy muck	41.4	.97	6.2
Sandy loam	43.3	2.40	7.8
Very fertile calcareous soil	38.3	3.65	9.8
Peat soil	274.0	20.6	49.7

From this table it is evident that hygroscopic water is not sufficient to supply the needs of a plant, but it indicates also that the plant can exist on a relatively small amount of water. In comparison with the moisture content at which wilting occurs, the amount present in the soil at the critical moisture content is large indeed, and seems to be entirely sufficient for good plant growth. A possible objection is that the optimum water content is not the same for all plants, but from the above consideration it is evident that at the critical water content enough water is present for a good, if not an optimum, plant growth. In further experiments on two soils in continuation of the experiments just described the wilting points were determined for a large number of field crops. These results are given in Table XXXVI.

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[a] Zweiter Ber. Landw. Vers.-Stat. Rostock, 1894, 19.

TABLE XXXVI.—*Moisture content at which wilting begins for two soils, according to Heinrich.*

Plant.	Moisture content at which plants begin to wilt.	
	On calcareous soil.	On peaty soil.
	Per cent.	*Per cent.*
Oats	8.4	3.23
Barley	9.98	33.3
Rye	9.55	32.8
Wheat		43.6
Corn	7.91	
French rye grass (*Arrhenatherum elatius*)		33.2
English rye grass		33.1
Meadow foxtail		34.2
Soft brome grass		32.8
Red clover	10.28	34.3
Sweet clover	8.77	
Lambs clover	9.24	
Crimson clover		34.1
Alfalfa	8.9	
Vetch		35.3
Esparcet	9.92	
Fire bean	11.04	
Horse bean	11.30	
Potatoes	5.07	41.4

Considering the possible variations due to the difficulty of making close representative moisture determinations in soils and the experimental difficulty of correctly judging the time of wilting, there is a striking agreement in the above results for various plants. The average for the calcareous soil is about 9 per cent of water, from which figure there is no striking variation in any of the cases considered, and the average for the peat is about 34 per cent of water.

The general belief that different plants require different optimum water contents in the soil seems to be a result of observations on the total amount of water that the plant actually requires rather than on the percentage in the soil best suited to its needs. The transpiration in one plant may be greater than in another, and the corresponding demand for water would be greater. Investigators in this field have usually supplied the extra amount of water demanded for this larger transpiration by increasing the total water content of the soil rather than by supplying more water as it is needed. That is, instead of gradually supplying a larger amount of water and maintaining the moisture content of the soil near a constant percentage, the same result is obtained by increasing the percentage of water in the soil at one time. The idea that there are different optimum water contents for the same soil for different plants may, therefore, be an outgrowth of the prevailing methods rather than of critical experimentation. Moreover, the idea that there are different optimum water contents corresponding to different plants has apparently been confused with the fact that some plants have more endurance under adverse moisture conditions than have others. These same plants may be able to grow in a large excess of water without great apparent injury, but actually require less for more favorable growth. The fact that one plant can tolerate larger amounts of water than another without serious injury does not alone justify the conclusion that the optimum water content differs for each.

From this work, showing the moisture content approximately constant with any one soil at which wilting of different plants begins and from the other considerations presented, it seems probable that the optimum water content is that which makes for the greatest aeration, loosest structure, and, in general, most favorable physical condition of the soil.

APPARATUS AND METHODS.

SCREENING APPARATUS.

In beginning work on penetration of soils in the loose condition, it was recognized that there existed a serious difficulty in obtaining a uniform packing and so arranging the conditions that the same grade of packing could be obtained on successive trials, thus insuring duplicate results. A preliminary investigation was made on the effect of packing on penetration. The firmness of the packing was determined from the weight of the soil, since the measurements were all made under one moisture condition and the soil was leveled in such a way that the same volume was always obtained. The change in packing was effected by jarring the dishes and by varying the method in which the soil was put into the containing vessel. The results of such a series of measurements on Leonardtown loam containing 9.1 per cent of water are given in Table XXXVII.

TABLE XXXVII.—*Influence of packing on penetration.*

Weight required for penetration.	Weight of soil.
Grams.	*Grams.*
70	1,785
75	1,808
85	1,830
113	1,902
175	1,965

When these results are plotted, using the weights of the soils as abscissas and the weights for penetration as ordinates, a smooth curve is obtained, showing that the penetration is not in direct proportion to the weight, but increases more rapidly. But for a small variation in packing, such as would be met under ordinary experimental conditions, the penetration is, for all practical purposes, a linear function of the packing. This is confirmed by the following measurements made on Leonardtown loam, which held about 15 per cent of water, its optimum water content.

TABLE XXXVIII.—*Influence of packing on penetration.*

Weight required for penetration.	Weight of soil.
Grams.	*Grams.*
64	1,702
71	1,719
87	1,739

These results when plotted lie on a straight line and indicate that soil variations or manipulations cause considerable differences in packing which, in turn, interfere with all measurements on penetration. The importance of having a satisfactory method of packing is therefore evident. Uniform packing is realized only when the process is entirely mechanical.

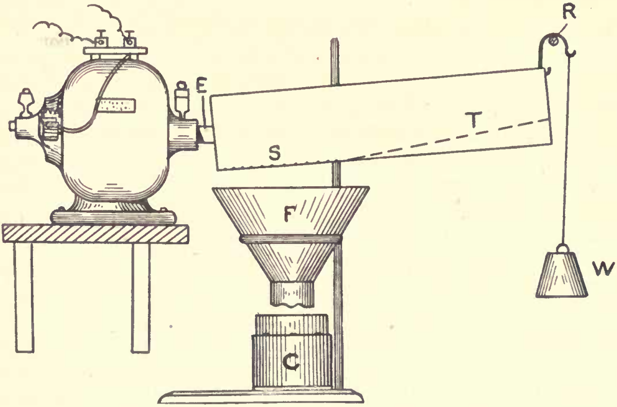

FIG. 27.—Apparatus for screening soils.

The apparatus finally used is shown in figure 27. To the shaft of an electric motor is fastened an eccentric *E*, made from a rod 2 centimeters in diameter, in which the shaft hole is drilled 0.5 centimeter off center. This eccentric fits into a hole in one end of the screen box *ST*. The motion of the revolving eccentric gives the screen a rapid shaking in both vertical and horizontal planes, which is very effective in forcing the damp soils through the mesh. The screen *S*, which is of 3 meshes to the centimeter, is in only one end of the box. A false bottom *T*, made of tin, serves to feed the material toward the mesh during shaking. The upper end of the box is supported by means of two hooks, resting on a horizontal rod *R*, shown in cross section in the figure. The hooks are made of heavy insulated electric-light wire, the covering of which serves to reduce the noise caused by rattling. Further, to prevent rattling at that end of the screen, a kilogram weight *W* is hung between the hooks. With this method of support the upper end of the screen is free to move, yet the motion is so reduced that during shaking the box stays well in position. The soil, after passing through the screen, falls into a funnel *F* and from there into the cup *C*, which holds the sample during the remainder of the experiment.

The cup proper is 12.5 centimeters in diameter and 9 centimeters high, having a capacity of 1,100 cubic centimeters. A rim is added, which makes it possible to fill the cup above its own level. The rim is then removed and the soil leveled off to the edge of the cup. This gives a more uniform packing in the upper layer of the soil.

The shaker makes it possible to repeat the packing of the same sample and also gives a basis of comparison in the measurements made on different samples, since the soil in each case is treated in the same way, falls through the same distance, and therefore is subjected to the same packing forces. Reproduction of these conditions is essential in a series of measurements made upon samples containing different quantities of water, where it is desirable that the only variable entering should be the water content.

PACKING APPARATUS.

The soil sample packed by the method just described is put into a uniform condition for experiment. Starting with the soil sample thus prepared it is possible to vary the packing in a definite and known way and thus study the effect of packing on the physical condition of the soil. The packing is done by the arrangement shown in figure 28, where a front and side elevation of the apparatus is shown. A vertical shaft of brass *AB* works easily through a wooden guide block *G*. On the bottom of the shaft is a circular plate *B* of hard rubber, just a little smaller than the inside of the cup *C*, into which it fits when packing the soil. On the upper end of the shaft is another plate *A*, which serves as a scale pan for the weights *W*, which are of lead and so made that they can be placed in the middle of *A* and concentric with one another, thus avoiding any serious side thrust where the rod passes through the guide. The shaft and plates are connected over pulleys with a weight *L*, by which they are balanced. In order to have the cup *C* still full after packing, a rim *R*, 4 centimeters high, is put on the cup. The screened soil is leveled to the upper edge of *R* and packed under any desired weight at a steady pressure for four minutes, after which the rim is removed and the soil surface reduced to the level of the cup proper. The sample is then ready for the penetration tests.

The behavior of the soil when packed in this way is indicated in figure 29, where a series of measurements for Podunk fine sandy loam containing 2.3 per cent water is shown. In addition to the packing caused by the soil falling from the screening machine, the soil was further compressed under pressure of 10, 30, and 50 grams per square centimeter. These pressures correspond to weights of 1, 3, and 5 kilos, the area of the compressing plate being about 100 square centimeters. The curve indicates that the increased packing pressure applied in this manner gives a fairly uniform increase in the force required for penetration.

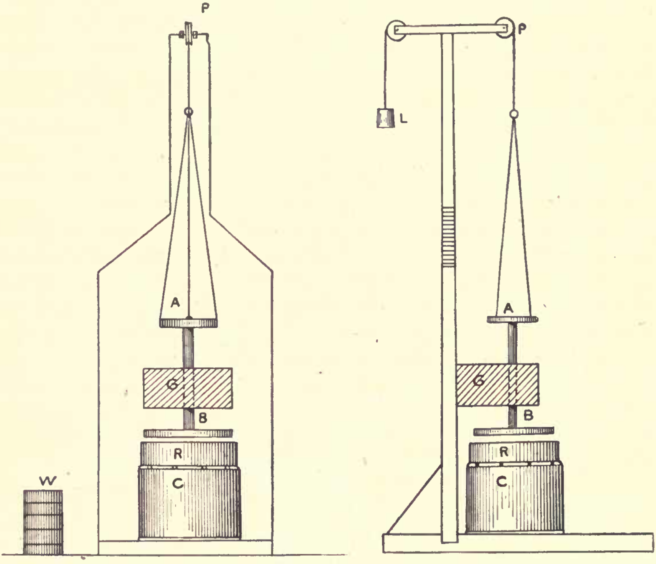

FIG. 28.—Apparatus for packing soils.

PENETRATION APPARATUS.

The force required for penetration was measured on the apparatus shown in figure 30. The penetrating tool A is made from a steel rod 1 centimeter in diameter. This is turned into the form of a cone 10.5 centimeters long and 1 centimeter in diameter in the thickest part. The large end of this cone terminates in a tongue which is so fastened to the scale beam AB that it is free to swing in the vertical plane of the beam. The beam itself, made of oak, is 140 centimeters long from the end A to D, the point of rotation. A counterweight W balances the beam and its attachments. Midway between A and D a pail P is hung, into which sand is run from a funnel F through a rubber tube closed by a pinchcock. This gives a method of constantly adding weight without jarring and of increasing the pressure to just the value necessary to force the tool into the soil to the required depth. The scale beam is guided beteween the upright parallel rods G, spaced to allow a free movement of the beam between them. M_1 and M_2 are clamps that check the up-and-down movement of the beam. The depth to which the point penetrates is determined by the position of M_2. The measurement is always begun at the same height—the level of the cup, which was also the soil level—and weight is added until the beam reaches M_2, by which time the tool has penetrated 6 centimeters into the soil. The approach of the beam to M_2 is observed by means of a small mirror R fastened at an angle to M_2.

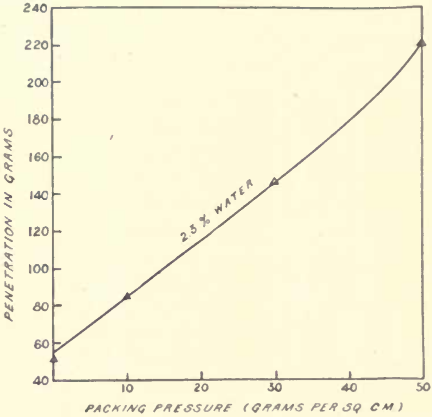

Fig. 29.—Penetration-packing results.

In making a penetration measurement the procedure is to make up a large soil sample to the desired water content, which is then determined accurately by drying a sample at 110° C. and calculating as per cent on the dry weight of soil. This method makes the different water contents of the same soil comparable one with another. The total sample is well mixed by screening and placed in a tightly covered pail. This holds enough soil to permit of repeating the measurements several times without twice using the same portion of soil. This is essential because a wet soil dries out quite rapidly when exposed to the open air, particularly during screening. By using a fresh portion each time successive measurements are made there will be but slight differences in the water content of the different samples. The soil is then leveled to the top rim by cutting off the extra material in such a way that no packing results, after which it is pressed, if desired, in the packing machine, the rim removed, and the soil again cut off to the level of the top of the cup. The penetration measurements are then made; generally three trials for each sample. They should be made at points the same distance from the rim of the vessel and equal distances apart. This condition is easily attained by drawing on the table a circle the size of the cup and eccentric to the point of the penetrating tool. The cup is so placed that it always coincides with this circle and between each measurement is rotated through 120 degrees. This method of spacing eliminates the personal factor of choosing the points for penetration and also makes the results more concordant. Since the soil in falling through the funnel of the shaking machine generally runs into the middle of the dish, from which point it spreads toward the sides, it tends to pack in the middle of the dish somewhat more closely than around the edges, so the packing at equal distances from the center is the same. After penetration the weight of the sand required to force the tool into the soil is determined. Since the pail is suspended in the middle of the beam, one-half the weight of the sand is the pressure applied in penetration. The cup and the soil are also weighed, the weight of the cup subtracted, and the specific gravity of the soil sample calculated from the volume of the cup.

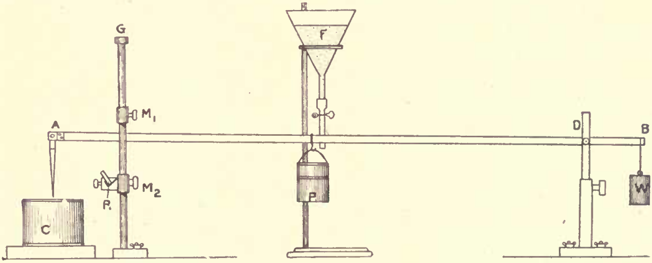

FIG. 30.—Apparatus for measuring penetration.

No difficulty is experienced in taking three penetration measurements on one dishful of soil. The three points at which the penetration tool enters the soil are far enough apart that the crowding aside of the soil at one point by the penetrating tool does not affect the following measurement at another point. Should it do so the force required for penetration would increase with each successive measurement, while as a matter of fact the variation is in no way regular between the different measurements.

APPARATUS FOR MEASURING VOLUME.

Preliminary method.

The first apparatus designed for volume measurements was not intended for very extended use, but rather as a convenient method of preliminary investigation. Some parts of it were used in subsequent investigations, and therefore a description of it is given here. The apparatus is illustrated in figure 31. The soil is contained in a glass tube *A*. For this purpose an Argand chimney has been found satisfactory and of suitable dimensions. In order to permit the wetting of the soil by capillarity the bottom of the tube *A* is closed by a ring *B*, made from a piece of brass tubing 2.5 centimeters long, with an inside diameter just a little larger than the outside diameter of the glass tube. A disk of brass gauze is soldered into the ring, as indicated in the diagram by the heavy dotted line. The ring is fastened to the tube by means of three set screws, one of which is indicated by *C*. In order to keep the finer soil particles from sifting through the brass gauze the end of the tube is covered by filter paper *D* before insertion into the ring. The dry soil is poured into the glass tube and then wetted by dipping the bottom of the container into water. Bearing on the upper surface of the soil is a brass tube *MN*, which works through a wooden guide block *E*. Changes in the volume of the soil cause, of course, a change in the level of the upper surface, and this change is communicated to the tube *MN*, and followed at *M* by a micrometer screw held firmly in place to the support of which *E* is a part. In order to hasten the drying the evaporation from the surface of the soil at *N* is increased by blowing a stream of air into the top of the tube. The air used for this purpose is passed through sulphuric acid in order to dry it. The drying progresses slowly owing to the small amount of surface exposed when *N* is in position. It is not feasible to remove *N* between measurements on account of the uncertainty of getting it back into the

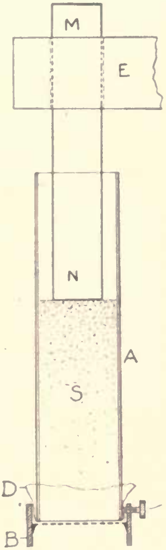

FIG. 31.—Apparatus for glass tube method of measuring changes in soil volumes.

same place when another measurement is to be made. As the drying occurs only at one end of the soil column an error is introduced, since the top of the soil was drier than the bottom. However, in a soil column of this length, if the drying proceeds slowly, this difference in moisture content of the top and the bottom is not very marked. More serious difficulty might be caused by the adhesion between the soil and surface of the glass, which would seriously cut down the influence of changing moisture content on the volume. It is evident from this preliminary attempt that a method suitable for accurate volume work should embody the following points: (1) In order to shorten the time required for carrying through one experiment it is essential that the drying out of the wet sample be rapid; this can be accomplished by exposing as great an area per unit volume of soil as possible. (2) The thickness of the soil from the drying surface down should be small in order that no large difference in moisture content may occur between the top and the bottom of the sample. (3) Since the change in volume is measured by the linear contraction it is essential to have the length in this one direction as great as possible. (4) The soil should be supported in such a way that after drying out it can be wetted again by capillarity without otherwise disturbing the sample, thus making it possible to use the same soil sample through several cycles of moisture change. (5) The soil sample should also be supported in such a way that it is independent of the measuring apparatus and movable at will, so that the same micrometer may be used to measure several samples drying out at the same time. These considerations led to the development of the "soil column method."

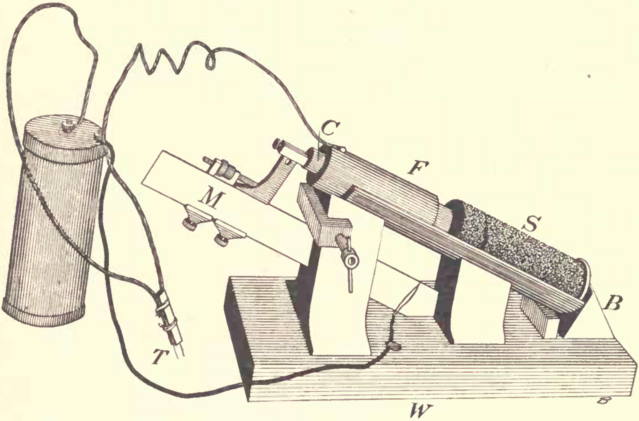

FIG. 32.—Apparatus for soil column method of measuring changes in soil volumes.

Soil column method.

The apparatus used in this method is shown in figure 32. The soil column *S* is molded in an apparatus similar to that shown in figure 31, where the soil is either put in dry and wetted by capillarity or packed into the tube in moderately moist condition, in which state it holds together well when pushed out of the tube onto the brass support shown in the figure. This support is made by cutting longitudinally a brass tube of a diameter a little larger than that of the soil column. Into one end of the support a circular brass disk is screwed so that it is perpendicular to the axis of the tube. Against this disk the lower end of the soil column rests. The disk is perforated so that a column can be wet by capillarity by simply dipping the lower end of its support into water, thus rewetting the sample without in any other way disturbing it. In this arrangement a large surface of soil is exposed to evaporation, and drying proceeds with considerable rapidity. A wet column of this kind reaches the air-dry condition in two to five days, depending on the nature of the soil. This method also insures a comparatively uniform moisture content from the top to the bottom of the sample. Resting against the upper end of the soil column is a brass follower *F* made from heavy brass tubing by inserting into the two ends pieces turned from solid brass. The part projecting from the lower end is made somewhat smaller than the tube so that it will not come in contact with the surface of the soil support, because upon contraction enough soil is left to roughen considerably this surface. The upper end contains a contact piece *C* turned from a brass rod. This is so arranged that by means of a screw, shown in the figure, it may be adjusted to lengthen or shorten the follower. By means of this adjustment the total length of the soil column and the follower can be made nearly the same in different samples, thus adapting the limits of the micrometer screw to their measurement. The Vernier scale and micrometer screw are shown at *M*. As the soil contracts during the wetting, the inclination of the support and the weight of the follower are sufficient to keep it pressed down against the end disk. The contraction of the soil therefore results in a downward movement, which is measured by the micrometer. In order to tell just when the micrometer comes in contact with the end of the follower at *C* an electrical contact device is used. One terminal of a battery is connected through an electric bell to *F*. When *M* makes the metallic connection at *C*, the circuit is closed and the bell rings. Instead of the bell the figure shows an arrangement *T* in which the two bare terminals are held at a short distance apart. By placing these two wires on the tongue, the instant of contact at *C* may be detected by a sharp acrid taste. This device is even more delicate and satisfactory than the bell. The contact can be determined with such precision that the readings taken at the same time show no variation within the limits of the micrometer used. The micrometer scale is held firmly in place by means of a screw clamp. The wooden support is sawed in such a way that the micrometer scale is slipped into position and a screw clamp pinches the two sections of the wooden support. The part of the apparatus consisting of the soil column and its follower can be lifted from the wooden supports without in any way affecting the soil sample. A different soil sample can be placed in position and measured by the same micrometer. At each measurement this movable part comes into the same position, for it is brought down firmly against the end block *B*. Since the wooden vertical supports are cut V shaped, the half-round section of brass tubing fits snugly into place.

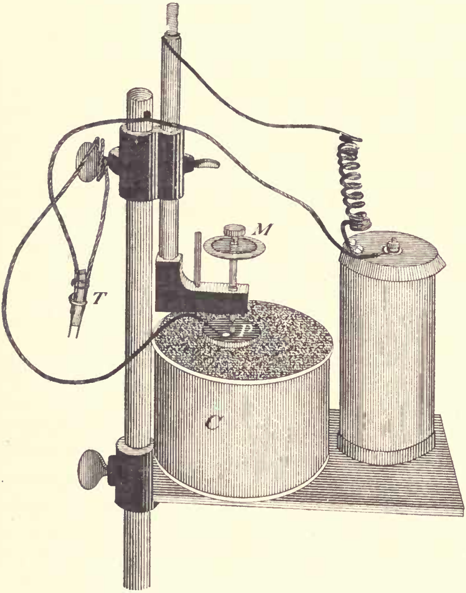

FIG. 33.—Apparatus for micrometer method of measuring changes in soil volumes.

This method has proved well suited to soils having the power to retain the form of the cylindrical soil column irrespective of the moisture content. Some soils, however, can not be successfully handled in this way, either because when wet they become incoherent and do not retain their form or because when dry they crumble. The method is not well suited for continued observations on wetting and drying of the same soil sample, because, as has been pointed out in a previous chapter, the volume changes tend to cause cracking of the soil; these cracks become points of weakness and in time cause the breaking down of the soil column.

Micrometer method.

In order to get around the difficulties just described the "micrometer method" was devised, in which the soil sample is better supported, being held in a cup. The form of apparatus is shown in figure 33. The soil sample is contained in a cup *C*, which has a perforated bottom through which the soil may be wetted. This cup rests directly on the metal table of an adjustable stand, to which the micrometer screw is also attached. This method of support has a distinct advantage, since there is little possibility of the table and micrometer changing their relative positions and thus affecting the results. The variation in the height of the soil surface is measured by means of the micrometer screw *M*. A brass plate *P* with a projecting short vertical shaft rests on the surface of the soil. The micrometer point is brought just into contact with the top of the shaft. The contact is determined in the same manner as described in the preceding method. In order to obtain a good electrical contact with the plate *P* without disturbing its position in any way, a drop of mercury is held in a depression drilled into the surface of the brass.

This method also permits measurements being made on a number of samples, since the cup *C* can be removed from the table and another cup inserted in its place without displacing the micrometer. The moisture content of the soil sample corresponding to the time of measurement is determined in both this and the soil column method by directly weighing the supporting dish, the dry soil equivalent being determined when the sample is first prepared. Although the micrometer screw used in this method measures to 0.0001 centimeter, measurements were ordinarily made only to 0.001. On account of the electrical conductivity of the moist soil and since the cup rests on the metallic table it is necessary to insulate the brass plate *P* from the soil. This is done by fastening a hard rubber disk to the underside of the plate. The same result can, of course, be obtained by insulating the cup *C* from the stand. In this method the amount of surface exposed to evaporation is not so large as in the soil column method, so that the time required for a series of measurements is somewhat longer. Because of the better support of the soil column this method is applicable to almost any soil and quite independent of errors due to a defective soil column. In any future work it would be well to use larger dishes; this would tend to reduce to a minimum any errors due to adhesion between the soil and the cup. A deeper dish may profitably be used, thus giving a larger linear change, but it must be not deep enough to cause a large difference in moisture content between the lower and upper soil layers.

Cathetometer method.

The cathetometer method closely resembles the micrometer method. The soil is contained in a similar dish and the up and down movements of a point fastened to a brass disk are measured by means of a cathetometer instead of a micrometer. This method is valuable as a check method, showing that the same results are obtained irrespective of the method used. It offers no particular advantage over the micrometer method and possesses some disadvantages. Since the cathetometer and the soil are placed several feet apart, they have no support in common, and a change of pressure on the floor may cause a variation in the level and a corresponding error in the readings obtained. Sighting the cross hairs of the cathetometer telescope on the point does not permit the same accuracy of reading as in case of the micrometer with the electric contact method. The finest graduations on the cathetometer used were 0.01 centimeter. This, added to the difficulty of reading mentioned above, made very accurate results impossible. This method might be improved by having the apparatus set up on a firm foundation, having better sighting device, larger dishes, etc., but the only advantage it can then offer over the micrometer method is that the plate on the soil surface would not be subject to any disturbing external pressure, such as might possibly be caused by the micrometer screw.

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BUREAU OF SOILS—BULLETIN No. 51.

MILTON WHITNEY, Chief

ABSORPTION OF VAPORS AND GASES BY SOILS.

BY

HARRISON E. PATTEN AND FRANCIS E. GALLAGHER.

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MILTON WHITNEY, Chief of Bureau.
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LETTER OF TRANSMITTAL

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., January 14, 1908.

Sir: I have the honor to transmit the manuscript of a technical article entitled "Absorption of Vapors and Gases by Soils," by Messrs. Harrison E. Patten and Francis E. Gallagher. It contains a historical review of the subject, together with experimental studies on the conditions which determine the quantity and rate of gaseous absorption by soils.

The article gives much valuable information which should be made available to the public. In accordance with your suggestion it has been gone over carefully with Assistant Secretary Hays, who authorizes me to state that he concurs in my recommendation for its publication.

Respectfully,

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

PREFACE.

In the continuation of the studies on absorption which have been carried on in this Bureau, it has been deemed desirable to direct attention especially to the absorption of gases by soils, and the present bulletin contains a description of certain special studies on this subject by Messrs. Patten and Gallagher.

That soils have a high absorptive power for gases, and show a direct selective absorption from gas mixtures as well as from liquid solutions, has long been known, and this fact has generally been recognized as having an important agricultural and geological significance. But up to the present it can not be said that agricultural investigators have given the question the consideration which its practical importance warrants.

In the present bulletin the absorption of the principal gases by various types of soils and the rate at which such absorption takes place have been brought out in such a manner that practical workers in soil problems will be able to use the results to advantage. Special significance must be attached to the absorption of water vapor, and in this bulletin the principal facts now known from the investigations of former workers or of the authors of the bulletin themselves are brought together in such shape that they are available not only for practical workers, but for the further investigation of scientific workers.

The relation between the absorption of water vapor on the one hand and the evaporation of water from that soil has been carefully investigated, and the laws controlling it have been clearly brought out; and the influence of soluble materials contained in the soil as affecting these laws has been shown. The significance of cultural methods as affecting either the absorption of water vapor or its evaporation has been shown. And finally, the important practical fact has been established that the wilting point—or that water content of the soil at which plants can no longer thrive and which has been shown elsewhere to be a physical factor of the soil—marks a water content higher than that which the soil can attain by direct absorption from a humid atmosphere, even though this latter be maintained at the point of saturation.

The laws governing the absorption of other gases or vapors appea in general to be very similar to those governing the absorption water vapor, and it may now be safely claimed that the broad subjec of absorption of vapors by soils has been brought to a satisfactor state as regards not only our theoretical knowledge of the principl involved and their importance to practical agriculture, but also they bear upon the practical methods of control.

FRANK K. CAMERON.

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ABSORPTION OF VAPORS AND GASES BY SOILS.

PREVIOUS WORK.

INTRODUCTION.

It is well known that charcoal absorbs enormous volumes of gases from putrefying animal matter, and the similar power of soils to take up odors from excreta has been utilized from the earliest times.

The term *absorption* includes adsorption upon the surface, possible penetration of vapor into the solid, and retention of liquid in the angles formed between adjoining particles. A short review of the development of our knowledge of gaseous absorption is helpful here in bringing to mind the experimental facts and the varying explanations offered in connection therewith.

ABSORPTION OF GASES.

Fontana in 1777 established the fact that numerous porous bodies retain gases upon their internal surface, but did not deduce regularities from his data.

Morozzo, Rouppe, and Norden[a] confirmed his observations in 1800, but de Saussure,[b] during 1812 to 1814, was the first to investigate this field extensively. He heated his absorbent material to redness before using, to expel residual gases, and then subjected the weighed absorbent to the action of a gas, under known temperature and pressure conditions. He drew the following conclusions: (1) The porous bodies investigated absorb gases; (2) the degree of absorption varies with the form and magnitude of the pores; (3) different substances possess a different absorption capacity; (4) the same substance absorbs different quantities of different gases; (5) easily condensed gases are in general absorbed more easily; (6) absorption decreases as temperature increases; (7) at higher pressure more gas is absorbed than at lower pressure; (8) heat is evolved during the process of absorption.

To these fundamental observations Smith[c] adds: (1) Charcoal exercises a selective absorption toward mixtures of gases; for a con-

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[a] O. Lehmann, Molekular-physik, II part, 83.

[b] Ann. Phys. Gilbert, **47**, 113 (1814).

[c] Ann. Chem., Suppl. **2**, 262 (1862-1863).

siderable time oxygen alone is absorbed from air; (2) charcoal satu
rated with nitrogen and then placed in other gases first gives up
part of the nitrogen before absorbing the second gas; (3) charcoa
saturated with oxygen does not give up the gas, either upon warmin
or treatment with boiling water, but under these conditions carbo
dioxide is evolved rather than oxygen.

Stenhouse,[a] too, has studied the absorption of gases by charcoa
made from various materials; his figures, given in Table I, represen
the number of cubic centimeters of gas absorbed by 1 gram of char
coal. Wood charcoal shows a higher absorption for the gases use
than does peat or animal charcoal, with the exception of hydro
chloric acid gas, which is taken up in greater volume by peat.

Table I.—*Absorption of gases by charcoal, according to Stenhouse.*

Gas.	Kind of charcoal.		
	Wood.	Peat.	Anima
	C. c.	*C. c.*	*C. c*
Ammonia	98.5	96.0	43
Hydrochloric acid	45.0	60.0	....
Sulphurous	32.5	27.5	17
Carbonic acid	14.0	10.0	5
Oxygen	0.8	0.6	0

Dewar[b] has found that charcoal and lampblack are nearly equal i
absorbing power for gases at the temperature of liquid air, and tha
graphite is only one-fourth as good an absorbent.

ABSORPTION OF AIR.

Reichardt and Blumtritt[c] showed that nitrogen is absorbed to
much greater extent by soils and soil constitutents than is oxyge
and that each gas is retained to a different degree by different sub
stances—a clear indication of the selective power which solids an
gases mutually exert in absorption reactions.

ABSORPTION OF WATER VAPOR BY SOILS.

When a soil is saturated with water by rain, part of the water pe
colates away to lower levels, and another part of the water evaporat
from the surface.

With a view to correlating the capacity of soils to resist dryin
out, with their composition and with their productiveness, Schüble
determined the water vapor absorbed by various soils and soil co
stitutents from a nearly saturated atmosphere during 24 hours. Th
absorption process is evidently the reverse of drying out, but gives

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[a] Cited by Johnson, How Crops Feed, p. 160.

[b] Chem. News, **94,** 174 (1906); Proc. Roy. Soc., **74,** 130 (1904).

[c] Jour. prakt. Chem., **98,** 476 (1866).

[d] Cited by Johnson, How Crops Feed, pp. 161–162, 1870.

measure of the speed with which a dry soil takes up the first portions of water vapor, and this speed is clearly an indication of the strength with which the water is held by each soil. Thus, he found that 1,000 parts of soil absorbed parts of water as follows: Quartz sand, coarse, 0; gypsum, 1; calcareous sand, 3; plow land, 23; clay soil (60 per cent clay), 28; slaty marl, 33; loam, 35; fine carbonate of lime, 35; heavy clay soil (80 per cent clay), 41; garden mold (7 per cent humus), 52; pure clay, 49; carbonate of magnesia (fine powder), 82; humus, 120.

Similarly Davy[a] gives the quantity of moisture taken up during one hour exposure to the air by soils which had been dried at 212° F. as follows, in parts of water per 1,000 parts of soil: Sterile soil of Bagshot heath, 3; coarse sand, 8; fine sand, 11; soil from Mercy, Essex, 13; very fertile alluvium, Somersetshire, 16; extremely fertile soil of Ormiston, East Lothian, 18.

From these results it may be concluded that the absorptive capacity of soil for water vapor is generally higher the finer the texture of the soil and the greater its content of humus. It appears, too, that productive soils have a very considerable capacity for water vapor, while the poor soils range much lower.

Regarding the effect of temperature upon the quantity of water vapor absorbed, Knop[a] has shown that at higher temperature the absorption is very considerably decreased. A sandy soil from Moeckern, Saxony, absorbed in parts of water per 1,000 parts of soil the following quantities of moisture: At 55° F., 13; at 66°, 11.9; at 77°, 10.2; at 88°, 8.7.

The experiments of Ammon[b] likewise show that the absorption of water vapor by soil constituents decreases as the temperature rises. The relative absorption at any one temperature of the substances used decreases in the order, ferric hydroxide, humus, kaolin, calcium carbonate, gypsum.

Von Dobeneck[c] has studied in great detail the conditions which determine the absorption of water vapor and gases in general by various soil constituents and admixtures of the same, with the following results: (1) The absorption is greater the finer the particles of the solid; but this increase is not directly proportional to the increase in surface, since large grains absorb relatively more gas than would be expected from the surface exposed. It should be remembered, however, that great error is introduced when the surface of a powder is calculated from the average diameter of its granules. (2) He found that adsorption and hygroscopic retention of moisture upon surfaces, which were then looked upon as different, are subject to the same controlling conditions. (3) The different soil constituents all possess a considerable absorption capacity, but gases are absorbed to a different degree by each solid substance. (4) Mixtures of these soil constituents absorb gases additively; that is, each soil material exerts its absorptive effect independently of the rest of the soil about it. (5) Absorption decreases with rise in temperature and is very nearly proportional to the reciprocal of the partial pressure. (6) For atmospheres of the same relative humidity, the temperature has little effect upon the mass of water absorbed; the absorption increases with increasing relative humidity, and at 20° C. the rise in absorption for equal per cent increments in the relative humidity is greater the nearer the interval lies to the point of saturation (100 per cent humidity). (7) Soil constituents moistened with water absorb gases in greater quantity than the same mass of water alone.

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[a] Cited by Johnson, How Crops Feed, pp. 161–162, 1870.

[b] Forsch. Agr.-Phys., **2**, 36 (1879).

[c] Forsch. Agr.-Phys., **15**, 163 (1892).

Van Bemmelen[a] has determined the absorption of water vapor by soils and inorganic oxides, especially such as yield gelatinous hydrates with water, with reference to (1) the influence of original water contained in the soil or solid oxide upon the quantity of water it can yet absorb; (2) the effect of vapor pressure upon absorption and liberation of moisture; (3) the structure and history of the oxide as related to its absorptive power. He used the oxides, SiO_2, SnO_2, MnO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, BeO, MgO, and CuO and various soils. His results in general indicate that the absorption of water vapor increases with the vapor pressure, but is not simply proportional to it; that the fineness of the grains of a partially hydrated oxide has little influence upon its absorption—an effect to be expected where imbibition takes place; that the moist oxides expand as more water is absorbed and contract as this water evaporates from them in an atmosphere of lower vapor pressure; that some oxides form a translucent jelly when they contain a certain quantity of water, and this translucence indicates that the jelly is made up of fine cells. He concludes that the existence of definite chemical hydrates in these noncrystalline jellies is as yet undemonstrated and extremely improbable.

Van Bemmelen's reason for so thoroughly investigating these gelatinous inorganic hydrates is that much of the absorptive power of a soil is due to their presence, occasioned by the disintegration of minerals subject to weathering. His results on the absorption of water vapor by soils are similar to those obtained with these inorganic oxides, and agree in general with the results of earlier investigators. Each soil shows its own peculiar power of absorbing water vapor—the finer the soil grains the greater the absorption; the presence of individual soil constituents of high absorptive power, of course, raises the absorption in proportion to the amount of each in the soil.

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[a] Zeit. anorg. Chem., **5**, 467 (1893); Ber. deutsch. chem. Ges., **13**, 1467 (1880); Jour. prakt. Chem., **23**, 324, 379 (1881); **26**, 227 (1882); Rec. Trav. Chim. Pays.-Bas, **7**, 1 (1888); Jour. prakt. Chem., **46**, 497 (1892); Zeit. anorg. Chem., **18**, 122 (1898); **20**, 185 (1899); **23**, 111–321 (1900); Sitzungsber. d. K. Akad. d. Wiss., Amsterdam, Nov. 26, 1902; Arch. Néel. (2), **10**, 267 (1906). See also Cross, On the Reformation of Hydrates, Jahresb., 1879, 179; also, Spring and Lucion, Zeit. anorg. Chem., **2**, 195 (1892).

According to Hilgard,[a] the hygroscopic moisture of a soil may vary from 2.48 per cent to 21 per cent, depending upon its composition. He has criticized the experiments of Schübler, Knop, and others, who found that absorption of water vapor decreases with rise in temperature. Hilgard finds that exactly the reverse is the case; soils exposed to an atmosphere saturated with water vapor absorb more moisture at high temperature than at low.

An attempt to discriminate between moisture held by a powder as "hygroscopic moisture" and water in the capillary spaces meets with difficulty.[b] We have no sharp experimental method of ascertaining what fraction of the water is retained on the surfaces of the grains. This is especially so as an even distribution of moisture throughout the powder is hard to secure, and failing of this the powder is balled together and holds part of the liquid in its capillary spaces between the grains.

Briggs[c] determined the quantity of water vapor absorbed by quartz grains of various degrees of fineness, and from the mechanical analysis of each powder calculated the surface presented, and thus found the thickness of the layer of adsorbed water. Assuming the density of the film as uniform and equal to unity and postulating an even distribution of the water over the entire surface, the maximum thickness obtained was 2.66×10^{-6} cm. in an atmosphere within 1 per cent of saturation at 30° C. He concludes that the adsorption is not due to soluble bodies present upon the surface of the quartz, as Warburg and Ihmori have suggested, but to the mutual attraction of quartz and water.

Parks[d] calculates the thickness of the water film upon glass wool as 13.3×10^{-6} at 15° C. Trouton[e] and O. Masson and E. S. Richards[f] have carefully determined the conditions under which cotton absorbs moisture. Trouton suggests that the water vapor is condensed to liquid upon the surface of the cotton. Masson and Richards find that cotton containing a definite proportion of moisture resembles an aqueous solution in that it exercises a vapor pressure which is at different temperatures a constant fraction of that of pure water.

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[a] "Soils," pp. 196, 198 (1906).

[b] Soyaka, Forsch. Agr.-Phys., **8**, 1 (1885); Whitney, Agricultural Science, **3**, 199 (1889); Katao, Ueber die Wasserbewegung in Boden, Bul. Col. Agr., Imp. Univ. Tokyo, Vol. 3, No. 1 (1897); Briggs, Bul. No. 10, U. S. Dept. of Agr., Division of Soils (1897).

[c] Jour. Phys. Chem., **9**, 617 (1905).

[d] Phil. Mag. (6) **5**, 519 (1903); also (6) **4**, 240 (1902).

[e] Proc. Roy. Soc. London, **77**, Ser. A, 292 (1906).

[f] Ibid., **78**, Ser. A, 412–429 (1906).

In this connection it is interesting to note that Bunsen[a] found that glass fiber continued to give up moisture on heating until a temperature of 503° C. was reached; similarly, Day and Allen state that a temperature of 600° to 800° C. (a low red heat) is required to remove hygroscopic moisture from minerals. From the fact that moisture is retained upon the surface of these substances at high temperature it may be inferred that the attraction between the substance and water is greater than the vapor pressure, which at such temperatures amounts to hundreds of atmospheres.

ABSORPTION OF WATER VAPOR.

STATEMENT OF THE PROBLEM.

The general problem before us is to find the relation of climatic humidity to soils. In nature a system is rarely in a state of equilibrium, and more or less rapid changes in the distribution of the constituents are in progress. Still, in the present instance, definite laboratory conditions for the equilibrium between soil moisture and water vapor in the air above it will afford a very fair approximation to field conditions, and by taking measurements upon the rate of approach to equilibrium we also secure an insight into the nature and rate of change in soil moisture during evaporation or absorption when sudden climatic changes disturb the approximate equilibrium between atmospheric moisture and soil moisture. Such displacement of equilibrium may be due to currents of air bringing a more or less humid atmosphere from a distance, or to heat changes accompanied by precipitation on cooling, or greater saturation capacity of the air for water on heating.

The first variation—change in humidity—may be experimentally reproduced by placing several equal portions of a soil of known moisture content in desiccators whose individual atmospheric humidity is maintained practically constant by sulphuric acid, differing in strength for each desiccator and thus giving a range of humidity from the very low partial pressure of concentrated acid to the vapor pressure of water at the temperature chosen for the experiments.

The second source of variation—heat changes—may be studied by running equilibrium experiments similar to those just described, but at different temperatures, and comparing the quantities of moisture in soil and in vapor above it at each of these temperatures.

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[a] Ann. Phys., **24,** 321 (1885).

[b] Pub. Carnegie Inst. of Washington, No. 31, pp. 56-57; Am. Jour. Sci. (4), **19,** 93 (1905).

EVAPORATION STUDIES.

Experimental methods.

The evaporation of water from soils was determined under different degrees of humidity, secured by maintaining the soils in small weighing bottles in desiccators containing sulphuric acid in varying concentration. Quantitative preliminary work showed the need of accurate temperature control; consequently the experiments here described were carried out in a double-walled air thermostat heated by incandescent electric lights, the current being controlled by a Geer thermoregulator[a] and the air circulated by an electric fan. (The temperature was recorded, when desired, by a thermograph. The temperature could thus be held constant and within 0.1° C. for days.)

Diffusion constant for the desiccators.

As regards the diffusion of water vapor from the soil in the weighing bottle through the atmosphere of the desiccator down to the surface of the sulphuric acid, it may be stated that in general this takes place at a very constant rate. This constancy will be evident from an inspection of the curves given in figures 1, 2, and 3, for the evaporation of soils in atmospheres of different degrees of humidity. As may be expected, these curves are linear during the time when evaporation is taking place from the larger soil tubes, but when the soil moisture begins to evaporate from the finer capillary spaces, the rate of evaporation, and consequently the diffusion constant itself, changes as evaporation proceeds. A variation in the value of this diffusion constant may also be due to a slight difference in the size of the mouths of the weighing bottles.

Experimental data.

The rate of approach to equilibrium of quartz flour, Podunk fine sandy loam, and Sea Island cotton soils over water and over sulphuric acid of different strengths at 25° C. is given in Tables II, III, and IV, respectively. The upper section of each table shows the loss of water from a wet soil as the evaporation proceeds, while the lower section gives the absorption by the same soil in dry condition under the same conditions of temperature and humidity. Thus if sufficient time be given, the same percentage of moisture will be found in the soil regardless of its previous moisture content; i. e., equilibrium is approached from both the wet side and the dry side. At the head of each column in the tables is given the strength of sulphuric acid expressed in percentage by weight and the corresponding partial pressure of water vapor in millimeters of mercury.[b] The evaporation data from the upper half of Tables II, III, and IV are plotted in figures 1, 2, and 3, for quartz, Podunk, and Sea Island soils, respectively, ordinates being percentage moisture in the soil reckoned upon its dry weight, and abscissas time in days.

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[a] Jour. Phys. Chem., 6, 85 (1902).

[b] Landolt and Börnstein, Tabellen.

TABLE II.—*Change in moisture content of quartz flour exposed to atmospheres of different humidity at 25° C.*

MOIST SOIL.

Strength of sulphuric acid, with equivalent partial pressure of water vapor.								Water alone.	
94 per cent = 0.10 mm.		55.4 per cent = 6.0 mm.		42.55 per cent = 12 mm.		29.84 per cent = 17.9 mm.		23.55 mm.	
Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.
Days.	*Per cent.*	*Days.*	*Per cent.*	*Days.*	*Per cent.*	*Days.*	*Per cent.*	*Days.*	*Per cent.*
0.00	30.00	0.00	30.00	0.00	30.00	0.00	30.00	0.00	30.0
.167	29.40	1.02	27.80	1.04	28.50	1.04	29.20	1.01	29.9
1.00	26.30	2.11	25.40	2.10	27.20	2.11	28.50	2.11	29.8
2.08	23.10	3.08	23.40	3.08	25.80	3.09	27.80	3.04	29.7
3.08	19.80	4.00	21.60	4.04	24.60	4.04	27.20	6.04	29.5
4.00	16.80	8.00	13.90	8.00	20.00	8.00	24.80	13.00	29.3
5.15	13.40	10.10	9.80	13.00	13.80	13.00	22.00	27.00	28.6
6.04	9.80	13.00	4.10	17.00	9.50	21.20	17.70	55.00	28.5
8.02	4.40	17.00	.10	19.20	6.90	23.00	14.30	97.00	25.4
9.05	1.90	33.00	.09	23.00	2.80	33.00	11.00		
9.87	.50			25.00	1.20	38.00	8.20		
10.13	.10			26.00	.20	46.00	4.30		
11.16	.10			27.00	.12	52.00	1.30		
17.00	.07			30.00	.12	97.00	.12		
33.00	.07			33.00	.11				

DRY SOIL.

0.0	0.10	0.0	0.1	0.0	0.10	0.0	0.10	0.0	0.10
1.0	.10	1.0	1	1.0	.10	1.0	.10	1.0	.20
13.0	.08	33.0	.1	33.0	.11	3.0	.10	2.0	.20
33.0	.07					97.0	.12	3.0	.20
								6.0	.30
								13.0	.30
								27.0	.40
								55.0	.42
								97.0	.61

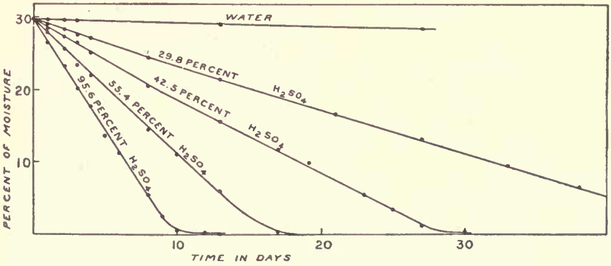

FIG. 1.—Curves for quartz flour, showing effect of humidity upon rate of evaporation.

TABLE III.—*Change in moisture content of Podunk fine sandy loam soil exposed to atmospheres of different humidity at 25° C.*

MOIST SOIL.

Strength of sulphuric acid, with equivalent partial pressure of water vapor.								Water alone.	
95.6 per cent =0.10 mm.		55.4 per cent =6.0 mm.		42.55 per cent =12 mm.		29.84 per cent =17.9 mm.		23.55 mm.	
Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.
Days.	*Per cent.*	*Days.*	*Per cent.*	*Days.*	*Per cent.*	*Days.*	*Per cent.*	*Days.*	*Per cent.*
0.00	30.00	0.00	30.0	0.00	30.00	0.00	30.00	0.00	30.0
.167	29.50	1.02	28.1	1.04	28.70	1.04	29.20	1.01	29.9
1.00	26.70	2.11	25.9	2.11	27.50	2.11	28.50	2.12	29.8
2.09	23.30	3.08	23.8	3.09	26.80	3.11	27.80	3.12	29.7
3.00	20.30	4.00	22.1	4.04	25.20	4.04	27.20	6.04	29.5
4.00	17.90	8.00	14.8	8.00	20.60	8.00	24.60	13.00	29.2
5.15	13.90	9.10	11.2	13.00	15.70	13.00	21.60	27.00	28.6
6.04	11.50	13.00	6.0	17.00	11.90	21.20	16.80	55.00	27.5
8.02	5.60	17.00	.4	19.20	9.80	23.00	13.30	97.00	26.5
9.05	2.50	33.00	.3	23.00	5.70	33.00	9.70		
9.87	.70			25.00	3.50	38.00	6.50		
10.13	.40			27.00	1.10	46.00	2.50		
11.16	.30			30.00	.40	52.00	.60		
17.00	.13			33.00	.43	97.00	.51		
33.00	.04								

DRY SOIL.

0.0	0.30	0.0	0.3	0.0	0.3	0.0	0.30	1.01	0.30
1.0	.30	1.0	.4	1.0	.4	1.0	.50	2.12	.70
13.0	.16	10.0	.4	33.0	.4	3.0	.51	3.12	.70
17.0	.13	33.0	.3			97.0	.48	6.04	.80
21.0	.03							13.00	.90
33.0	.02							27.00	1.00
								55.00	1.10
								97.00	1.16
									1.24

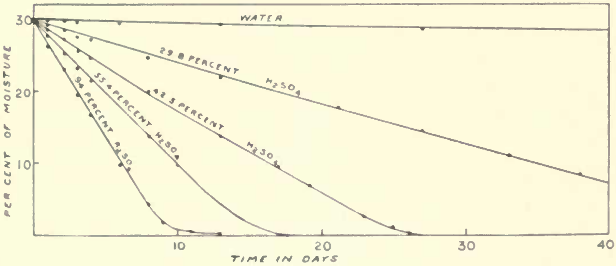

FIG. 2.—Curves for Podunk soil, showing effect of humidity upon rate of evaporation.

TABLE IV.—*Change in moisture content of Sea Island cotton soil exposed to atmospheres of different humidity at 25° C.*

MOIST SOIL.

Strength of sulphuric acid, with equivalent partial pressure of water vapor.								Water alone.	
94 per cent =0.10 mm.		55.4 per cent =6.0 mm.		42.55 per cent =12 mm.		29.84 per cent =17.9 mm.		23.55 mm.	
Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.	Period.	Moisture content.
Days.	*Per cent.*	*Days.*	*Per cent.*	*Days.*	*Per cent.*	*Days.*	*Per cent.*	*Days.*	*Per cent*
0.00	55.00	0.00	55.0	0.00	55.0	0.00	55.00	0.00	55.0
.167	54.20	1.01	52.9	1.04	53.2	1.03	54.10	1.10	54.8
.96	51.60	2.10	50.5	2.09	51.4	2.11	53.30	2.11	54.7
2.08	48.60	3.08	48.4	3.08	49.8	3.09	52.10	3.14	54.6
3.08	45.60	4.00	46.5	4.04	48.3	4.04	51.90	6.04	54.3
4.00	43.20	8.00	37.4	8.00	42.1	8.00	49.30	8.00	54.0
5.15	40.10	10.10	33.1	13.00	35.0	13.00	46.30	10.10	53.9
6.04	37.50	13.00	27.6	17.00	29.4	21.20	41.20	13.00	53.7
8.02	30.00	17.00	17.6	19.20	26.1	27.00	37.70	27.00	53.1
9.05	27.00	19.20	11.2	23.00	20.4	33.00	34.10	55.00	49.2
9.87	24.00	23.00	4.6	27.00	15.0	46.00	25.50	97.00	48.5
11.16	17.90	25.00	3.5	30.00	10.5	52.00	21.52	....	....
12.08	13.70	27.00	3.1	33.00	6.6	97.00	6.08	....	....
13.05	9.20	30.00	2.9	38.00	4.7	....	....	....	....
14.00	6.40	33.00	2.9	46.00	4.4	....	....	....	....
17.00	2.10	52.00	2.8	52.00	4.2	....	....	....	....
21.00	.98	....	....	....	....	....	....	....	....
33.00	.34	....	....	....	....	....	....	....	....

DRY SOIL.

0.0	4.40	0.0	4.4	0.0	4.4	0.0	4.4	0.00	4.4
1.0	4.10	1.0	4.6	1.0	4.7	1.0	4.9	1.01	5.1
13.0	2.90	13.0	4.8	13.0	4.9	3.0	5.4	2.13	5.6
17.0	1.70	33.0	2.9	21.0	4.1	4.0	5.5	3.12	5.9
21.0	1.00	52.0	2.8	....	....	13.0	5.9	4.04	6.1
33.0	.47	....	....	....	....	21.0	6.0	6.00	6.6
....	....	....	....	....	....	97.0	5.6	8.00	6.8
....	....	....	....	....	....	....	....	10.10	7.2
....	....	....	....	....	....	....	....	13.00	7.6
....	....	....	....	....	....	....	....	27.00	8.6
....	....	....	....	....	....	....	....	55.00	9.2
....	....	....	....	....	....	....	....	97.00	9.7

Discussion.

Evaporation from soils under different conditions of humidity in general proceeds regularly, as shown by the above curves, which are similar in form. The curves for Sea Island soil over 55.4 per cent sulphuric acid and over the concentrated acid (fig. 3) are displaced to the left in their lower portions. This effect is almost certainly due to the fact that the samples of quartz, Sea Island, and Podunk soils were run in the same desiccator. The latter two soils holding less water, reached the dry state first, and when they no longer gave up water to the surrounding atmosphere the rate of evaporation for Sea Island cotton soil increased, thus producing the displacement in the curve. This observation emphasizes the necessity of closely regulating the conditions for evaporation studies.

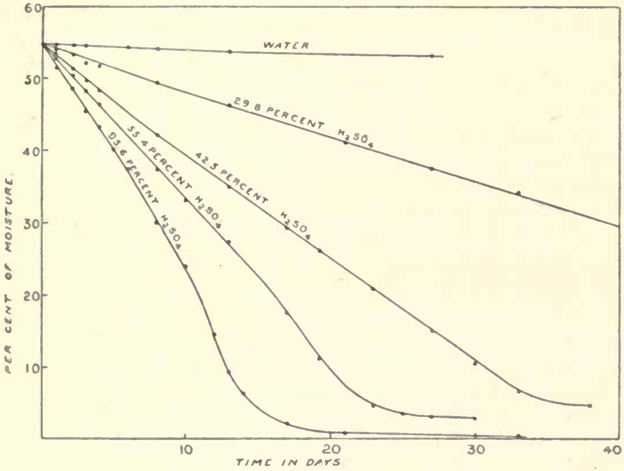

FIG. 3.—Curves for Sea Island cotton soil, showing effect of humidity upon rate of evaporation.

The influence of the presence of organic matter in a soil is shown by a comparison of the evaporation curves for quartz, Podunk, and Sea Island soils over concentrated sulphuric acid. The presence of organic matter in Sea Island soil increases its water-holding power some 25 per cent above that of quartz or Podunk soil, but it does not decrease the rate of evaporation, for the Sea Island curves are very nearly parallel to those for Podunk fine sandy loam and for quartz.

The foregoing study is important in that it gives a valid basis for applying the experimental results determined for one humidity condition to any other humidity condition. Because of the high rate of evaporation and slow change in vapor pressure of the acid, it is preferable to use concentrated sulphuric acid in evaporation studies. Results thus obtained may be confidently used for general application.

The relation of the length of time required for a soil to dry out to the atmospheric humidity is of great agricultural interest. Equal changes in humidity correspond to very unequal periods required for a soil to dry. Thus, for quartz, 60 days would be required to reach an air-dry condition with an atmospheric humidity of 75 per cent: 26 days with 50 per cent humidity; 16 days with 25 per cent humidity, and the proportionately long period of 10 days with 1 per cent humidity.

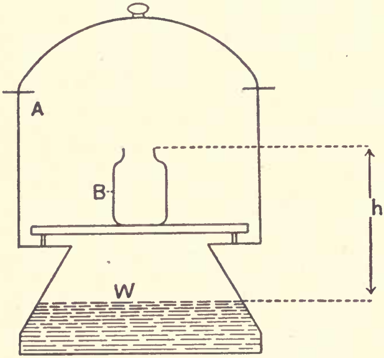

FIG. 4.—Drawing of desiccator containing soil sample.

The rate of evaporation curves show, too, that wet soil in an atmosphere saturated with water vapor slowly loses weight. This loss may be due to several disturbing influences.

There is a slight difference in the vapor pressure of the water in the bottle B and the water W, caused by the weight of a column of vapor of height *h* (see fig. 4). $P_b - P_w = hd$, where P_b and P_w are the vapor pressures at the level in the bottle and at the lower water surface W, respectively, and *d* is the density of the vapor. Although this value is very small, it is theoretically of interest and might enter into calculation when the time factor is large.

Small changes in temperature would cause loss of water from the weighing bottle containing moist soil. If the temperature rises a little this will first affect the desiccator near the outside wall, at A, figure 4. The increase in temperature momentarily reduces the relative humidity, thus disturbing the equilibrium. In order to restore equilibrium water vapor moves from the interior of the desiccator near B toward A. This produces at the same time evaporation of the water in B and of the water at W in the bottom of the desiccator. If a slight drop in the temperature within the thermostat now takes place cooling will first occur at A, followed by supersaturation and finally by condensation of moisture at A until equilibrium is again established. This cooling, however, will not produce a condensation upon the surface of the soil equal in amount to the loss by evaporation due to rise in temperature. Thus a slow loss of water from soil will result.

The thermostat was heated by an incandescent electric lamp, consequently a black soil might absorb sufficient radiant energy to maintain its temperature slightly above that of the surrounding medium. The vapor pressure of the warmer soil moisture would be higher, and a distillation of water from B to W would result.

Opening the desiccator for estimation of the moisture in soil would reduce the humidity and cause evaporation from the soil when replaced after weighing.

ABSORPTION STUDIES.

Experimental data.

The absorption of moisture by air-dry soils in an atmosphere saturated with water vapor is shown by the data given in Tables II, III, and IV for quartz, Podunk fine sandy loam, and Sea Island cotton soils at 25° C. As stated above, these experiments were carried out with weighing bottles placed in a desiccator. A parallel set of experiments using shallow aluminum dishes showed that the dishes do not give so great gain in moisture as is obtained when weighing bottles are used. The three soils used here were in air-dry condition at the start; their moisture content in percentage is given in Tables II, III, and IV.

A set of absorption experiments was carried out, using other soils and soil separates which had been heated to constant weight at 110° C. and then placed in a saturated atmosphere at 28° C. This set was not subjected to such accurate temperature control as those given above, still the curves obtained by plotting gain in moisture against time of absorption are very regular and the data fairly characteristic. The data are given in Table V.

TABLE V.—*Water vapor absorbed by soils from a saturated atmosphere at 28° C.*

Period.	Galveston clay.	Hagerstown loam.	Marshall silt loam.	Norfolk sand.	Quartz.
Days.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1	4.699	1.717	1.823	0.169	0.144
2	5.896	2.047	2.220	.220	.203
3	6.504	2.363	2.455	.240	.245
14	8.928	3.152	2.900	.322	.417
19	9.685	3.317	3.160	.334	.420
23	9.779	3.625	3.384	.354	.502
31	10.228	3.974	3.603	.390	.574
34	10.277	4.014	3.611		
37	10.373	4.107	3.713	.416	.625
49	10.841	4.553	4.005	.440	.752
AREA PER GRAM.					
	Sq. cm.	*Sq. cm.*	*Sq. cm.*	*Sq. cm.*	*Sq. cm.*
	3,280	2,270	2,320	300	1,260

Discussion.

At the bottom of Table V is given the area of each soil in square centimeters per gram as calculated from its mechanical analysis. This affords a rough comparison of soil texture with absorptive power, and shows that in a broad way the absorptive power is greater for soils of fine texture, as would be expected. Galveston clay absorbs three times the mass of water vapor that Marshall silt loam takes up, while the calculated area of the clay per gram is not three times greater, but less than a third greater, than for the silt loam.

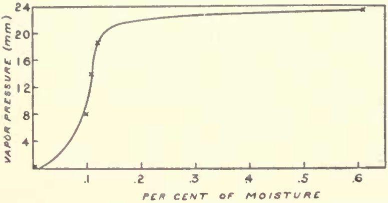

Fig. 5.—Curve showing variation of moisture in quartz flour with increase in atmospheric humidity.

DEPENDENCE OF MOISTURE CONTENT UPON HUMIDITY.

Table VI contains a summary of the equilibrium points already given in Tables II, III, and IV—that is, the percentage of moisture retained by each soil over each strength of sulphuric acid, a quantity which is practically the same as the per centage absorbed by the air-dry soil from air saturated with moisture over the different concentrations of sulphuric acid used. Of course, during the evaporation from the moist soil the sulphuric acid in each desiccator became diluted. In Table VI is given the initial and final strength of each portion of acid and the corresponding partial pressures of water vapor over this acid. Opposite these acid percentages are found the moisture contents of each soil, quartz, Podunk, and Sea Island.

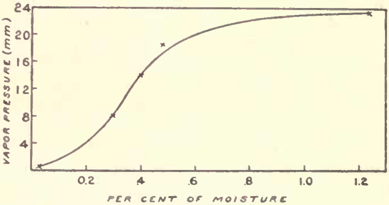

Fig. 6.—Curve showing variation of moisture in Podunk soil with increase in atmospheric humidity.

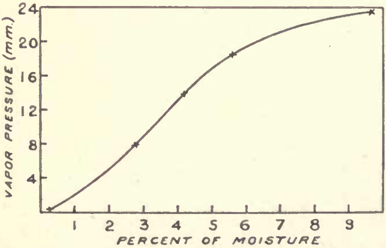

Fig. 7.—Curve showing variation of moisture in Sea Island cotton soil with increase in atmospheric humidity.

In figures 5, 6, and 7 curves are plotted from the data given in Table VI, showing the variation in moisture content of each soil with increasing atmospheric humidity. Ordinates are in partial pressures of water vapor expressed in millimeters of mercury; abscissas percentage of water in the soil.

TABLE VI.—*Variation of moisture content of soil with humidity under equilibrium conditions at 25° C.*

Strength of sulphuric acid.				Quartz.		Podunk.		Sea Island.	
Initial.		Final.		Drying out.	Absorbing moisture.	Drying out.	Absorbing moisture.	Drying out.	Absorbing moisture.
Per cent	*Mm.*	*Per cent*	*Mm.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
94.00	0.01	88.3	0.09	0.07	0.07	0.04	0.02	0.34	0.47
55.40	6.00	51.2	8.00	.09	.10	.30	.30	2.80	2.80
42.55	12.00	39.0	14.00	.11	.11	.43	.40	4.20	4.10
29.84	17.90	27.1	18.30	.12	.12	.51	.48	6.08	5.60
Water.	23.50	Water.	23.50	....	.61	....	1.24	....	9.70

The point on each of these curves figures 5, 6, and 7 corresponding to 23.5 mm., the partial pressure of water vapor at 25° C., may be high on account of the "dew point" effect produced by even slight temperature changes, as suggested in the previous discussion.

Because of the wide range through which the moisture content varies, the curve for Sea Island cotton soil in figure 7 is probably the most correctly determined. Owing to its low percentage of absorbed water, errors caused by slight temperature changes are greater relatively for quartz, and its curve in figure 5 is less accurate. These curves in figures 5, 6, and 7 resemble those given by van Bemmelen[a] for the absorption of water vapor by silicic acid at various partial pressures, save that for these soils no certain hysteresis effect is shown. However, we are here dealing with an adsorption effect rather than with imbibition, especially in the case of quartz flour; whereas van Bemmelen's hysteresis effect occurs with the colloidal silicic acid and is due mainly to imbibition; indeed, he gives data showing that the fineness of the silicic acid particles has no marked effect upon the mass of water vapor absorbed.

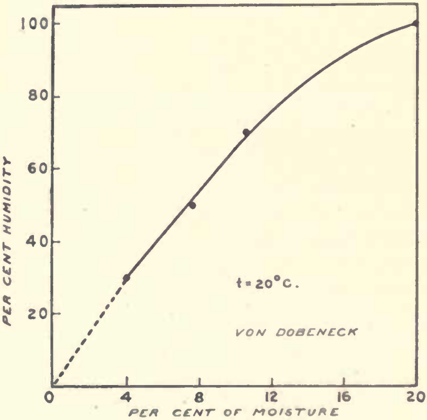

FIG. 8.—Curve showing variation of moisture in humus with increase in atmospheric humidity.

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[a] Zeit. anorg. Chem., 13, 233 (1896–97).

For comparison with this data, von Dobeneck's work upon the absorption of water vapor by humus in atmospheres of different humidity is given in Table VII. The equilibrium points are plotted in figure 8 and give a curve similar in form to that in figure 6 for the Podunk soil.

TABLE VII.—*Change in moisture content of humus submitted to atmospheres of different degrees of humidity at 20° C., according to von Dobeneck.*

Humidity 30 per cent.		Humidity 50 per cent.		Humidity 70 per cent.		Humidity 90 per cent.		Humidity 100 per cent.	
Period.	Moisture absorbed.	Period.	Moisture absorbed.	Period.	Moisture absorbed.	Period.	Moisture absorbed.	Period.	Moisture absorbed.
Days.	*Per cent.*	*Days.*	*Per cent.*	*Days.*	*Per cent.*	*Days.*	*Per cent.*	*Days.*	*Per cent.*
1	1.68	1	[a] 4.91	1	[a] 8.03	1	[a] 10.85	1	[a] 16.11
2	2.96	2	5.77	2	8.47	2	11.28	2	16.49
3	3.47	3	6.41	3	8.74	3	11.65	3	16.75
4	3.62	4	6.96	4	9.00	4	12.06	4	16.93
5	3.68	5	7.36	5	9.31	5	12.48	5	17.09
6	3.73	6	7.60	6	9.51	6	12.96	6	17.29
7	3.80	7	7.63	7	9.70	7	13.44	7	17.50
8	3.94	8	7.68	8	9.77	8	13.94	8	17.71
9	3.99	9	7.74	9	9.94	9	14.28	9	17.83
10	4.01	10	7.75	10	10.16	10	14.56	10	17.85
11	4.03	11	7.76	11	10.27	11	14.95	11	17.89
12	4.05	....	....	12	10.32	12	15.24	12	17.90
....	....	....	....	13	10.47	13	15.27	13	17.96
....	....	....	....	14	10.42	14	15.36	14	18.02
....	....	....	....	15	10.48	15	15.44	....	....
....	....	....	....	16	10.54	16	15.49	....	....
....	....	....	....	17	10.57	17	15.55	....	....
....	....	....	....	18	10.58	18	15.59	....	....
....	....	....	....	19	10.59	19	15.63	....	....
....	....	....	....	20	10.58	20	15.67	....	....

[a] The sample of humus after being saturated in an atmosphere of a given degree of humidity was placed in an atmosphere of higher humidity and allowed to reach equilibrium. This process was continued up to an atmosphere of 100 per cent humidity.

ABSORPTION OF OTHER VAPORS.

In Table VIII is given the percentage of toluene ($C_6H_5.CH_3$) vapor absorbed by Galveston, Hagerstown, Marshall, and Norfolk soils and quartz from a saturated atmosphere at 28° C. Similarly, Table IX contains the percentage of ether taken up by the soils at 27° C. from an atmosphere consisting entirely of ether vapor. Comparing these results with those given in Table V it is seen that Galveston clay has the same relative absorptive power for toluene and for water, although the mass of water vapor retained is almost exactly twice that of the toluene. The Hagerstown, Marshall, and Norfolk soils absorb toluene vapor to the extent of slightly less than half the mass of water vapor each soil can take up. Galveston clay absorbs about one-half more ether than water by weight, while the reverse is true of Norfolk sand, and the other two soils take up about the same quantity of ether as of water. Table X gives the absorption of water, ether, and toluene vapors at 28° C. by a soil separate fraction obtained in the mechanical analysis of soils[a] whose grains varied from 0.1 to 0.05 mm. in diameter. Here the absorption of ether vapor is slightly higher than that of water, and the toluene considerably lower. Still the quantities of all three vapors absorbed are of the same order of magnitude.

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[a] See Bul. No. 24, Bureau of Soils, U. S. Dept. Agr. (1904).

TABLE VIII.—*Toluene vapor absorbed by soils from a saturated atmosphere at 28° C.*

Period.	Galveston clay.	Hagerstown loam.	Marshall silt loam.	Norfolk sand.	Quartz.
Hours.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
18.00	2.400	0.860	0.810	0.078	0.112
25.25	2.697	....	.853	.083	....
67.00	3.797	1.367	1.297	.117	.192
139.00	4.467	1.736	1.529	.138	.272
187.00	4.791	1.851	1.615	.167	.285
477.00	5.318	1.866	1.759	.185	.285

TABLE IX.—*Ether vapor absorbed by soils, at 27° C., 575 mm. pressure.*

Period.	Galveston clay.	Hagerstown loam.	Marshall silt loam.	Norfolk sand
Days.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
0.75	4.320	2.625	2.320	0.421
11.75	4.840	3.580	3.070	.459
16.75	5.015	3.82	3.310	.470
28.00	5.760	3.995	3.605	.618
31.00	5.870	4.371	3.895	.618

TABLE X.—*Absorption of water, ether, and toluene vapors by a soil separate (0.1–0.05 mm.), at 28° C.*

Period.	Toluene.	Ether.	Water.
Hours.	*Per cent.*	*Per cent.*	*Per cent.*
17.75	0.264	0.481	0.367
25.50	....	.515	.418
35.00	.343	....	....
42.75	....	.699	.539
106.75	.396	....	....
114.50	....	.763	.609
154.25	.405	....	....
162.00	....	....	.624
352.00	....	....	.718

ABSORPTION OF GASES.

Absorption of air.

Reichardt and Blumtritt [a] recovered the gas absorbed by various soils and soil constituents from the atmosphere and analyzed it to ascertain what proportion of each atmospheric gas was held fixed in the soil. Their results are given in Table XI, and show that nitrogen is absorbed to a much greater extent than oxygen, and that each gas is retained to a different degree by different substances, a clear indication of the selective power which solids and gases mutually exert in absorption.

Dewar [b] has shown that all the inert gases—argon, helium, neon, krypton—can be condensed in charcoal as effectively as ordinary gases at suitable pressure and temperature.

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[a] Jour. prakt. Chem., **98**, 476 (1866).

[b] Proc. Roy. Soc., **74**, 130 (1904).

TABLE XI.—*Absorption of atmospheric gases by various substances, according to Reichardt and Blumtritt.*

Substance.	Gas per 100 grams.	Ratio, by volume.		
		Nitrogen.	Oxygen.	CO_2.
	C. c.	*Per cent.*	*Per cent.*	*Per cent.*
Charcoal, air dry	164	100	0	0
Peat	162	44	5	51
Garden soil	14	65	2	33
$Fe(OH)_3$, air dry	375	26	4	70
Fe_2O_3, ignited	39	83	13	4
$Al(OH)_3$, air dry	69	41	0	59
Alumina, dried at 100° C	11	83	17	0
Clay	33	65	21	14
Clay, moistened	29	60	6	34
River silt	40	68	0	32
Magnesium carbonate	729	64	7	29
Gypsum, pulverized	17	81	19	0

Absorption of oxygen.

In addition to the experiments of de Saussure, Smith, Stenhouse, and Reichardt and Blumtritt, several series of investigations have been carried out upon the absorption of oxygen gas. Joulin,[a] working with ignited charcoal, found that oxygen was so quickly absorbed that measurements on the velocity of absorption were not possible with the means at his command. Baker[b] has shown that a temperature of 450° C. is required to recover the gas from charcoal which has absorbed dry oxygen, and that the gas thus obtained is mainly carbon monoxide, only a little carbon dioxide being formed. Dewar,[c] on the other hand, by using a low-temperature bath of liquid air has succeeded in absorbing in charcoal more oxygen than nitrogen from the atmosphere, and upon warming the charcoal to ordinary room temperature again a large part of this oxygen is liberated, along with nitrogen, thus affording a ready means of obtaining oxygen from air by simply repeating the absorption and liberation process till the oxygen has the desired degree of purity. Richards and Rogers,[d] too, have shown that zinc oxide derived from the nitrate, even when heated to very high temperatures, retains nitrogen and oxygen. Morse and Arbuckle[e] confirmed these results, but found no evidence supporting Richards and Rogers's conclusion that the absorbed oxygen escapes more readily than the nitrogen. The zinc oxide was heated by Morse and Arbuckle to a temperature sufficient to melt cast steel and still retained per gram of oxide some 0.3 c. c. of gas whose composition varied—the nitrogen between 64.32 and 68.18 per cent, and the oxygen correspondingly, while the total volume of occluded gas was very nearly constant for eight different experiments.

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[a] Compt. rend., **90**, 741 (1880).

[b] Jour. Chem. Soc., **51**, 249 (1887).

[c] Chem. News, **94**, 174 (1906).

[d] Proc. Am. Acad., **28**, 200 (1893).

[e] Am. Chem. Jour., **20**, 200 (1898).

Absorption of nitrogen.

The absorption of nitrogen by soils has been studied mostly in connection with the absorption of atmospheric gases. From the work of Reichardt and Blumtritt, cited above, it appears that in general nitrogen is absorbed by soils in greater quantity than oxygen. This fact is especially worthy of note, since the absorption of oxygen and nitrogen from air by water gives a higher ratio of oxygen to nitrogen in the solution than the 1 : 4 relation which exists in air. The explanation immediately suggested is that oxygen is converted to carbon dioxide in the soil by action of the decomposing organic matter. But the similar high absorptive power of aluminum hydroxide, ferric hydroxide, and magnesium carbonate for nitrogen indicates that this is a real phenomenon, since these substances have no way of masking their true absorptive power for oxygen by converting it chemically to carbon dioxide, as a soil does, or to other oxides. Gypsum, too, preserves the ratio 81 : 19 of nitrogen to oxygen when it absorbs these gases from the air.

Absorption of carbon dioxide.

The determination of the actual quantity of carbon dioxide taken up by a soil from air is difficult, since the absorbed oxygen acts upon the organic matter in the soil to yield carbon dioxide, and the decaying organic matter itself contains carbon and oxygen which adds still more carbon dioxide to the soil atmosphere. The absorption of carbon dioxide from an atmosphere containing this gas alone can be estimated by the reduction of vapor pressure, by a density determination of the gas, or by determining chemically its weight in a given volume of the gas before and after contact with the soil.

Reichardt and Blumtritt determined the per cent by volume of carbon dioxide absorbed by soils and soil constituents. They showed that it is probable that the oxygen of the absorbed air is converted to CO_2 in the peat; of 162 c. c. gas absorbed from air, 44 per cent appears as nitrogen, 5 per cent as oxygen and 51 per cent as carbon dioxide. A similar relation is seen for the garden soil, moistened clay, and river silt. The ignited ferric oxide and aluminum oxide both show higher absorption of oxygen than the hydrated oxides, and lower absorption of carbon dioxide. This indicates that the absorption of carbon dioxide is dependent to a considerable extent upon the presence of water in the absorbing material, further evidence being afforded by the higher absorption of carbon dioxide by the moist clay.

Scheermesser[a] has stated that the amount of carbon dioxide absorbed by a dry soil is proportional to the amount of ferric oxide present, which would appear to be a generalization based on too few observations. Von Dobeneck[a] gives the carbon dioxide absorbed by soil constituents as follows:

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[a] Inaug.-Diss. Jena, 1871; ref. Chem. Centr., 1871, 462.

TABLE XII.—*Absorption of carbon dioxide by soil constituents according to von Dobeneck.*

Soil constituents. 100 grams.	CO_2 absorbed at—			
	0° C.	10° C.	20° C.	30° C.
	Grams.	*Grams.*	*Grams.*	*Grams.*
Quartz	0.023	0.021	0.023	0.022
Kaolin	.329	.298	.261	.215
Humus	2.501	2.125	1.773	1.479
$Fe(OH)_3$	6.975	5.702	5.054	4.274
$CaCO_3$	.028	.053	.034	.019

Kayser[b] attempted to express in absolute units the dependence of the absorption by glass fiber upon temperature and pressure. His aim was to measure the quantity of gas condensed by a known surface under definite temperature and pressure (and therefore with known concentration of the vapor phase) and to utilize this relation to estimate the surface of fine powders from the quantity of gas they absorb. But he was forced to abandon this, since adsorption is not dependent solely upon extent of surface, temperature, and pressure. He found (1) that glass fiber dried for a long time at high temperature adsorbs carbon dioxide, a few hours being required for saturation; (2) the adsorption increases with the pressure, and (3) decreases as the temperature increases.

A little later Bunsen,[c] using similar materials (glass fiber and carbon dioxide), obtained results at variance with those of Kayser, as follows: (1) Glass is not saturated with carbon dioxide in days or months, but only after several years have elapsed. Thus 1 sq. cm. of glass adsorbed of carbon dioxide at the end of the first year, 3.15 c. c.; second year, 1.10 c. c. more; third year, 0.88 c. c. more. (2) Sudden pressure and temperature changes never produced a noticeable evaporation of adsorbed carbon dioxide. (3) Sudden change of pressure within one atmosphere showed no effect upon the steady course of adsorption. (4) Within a temperature interval of 0.8° to 23° C., rise in temperature favored adsorption and conversely.

Bunsen[d] then showed that the difference between his results and those of Kayser lay in the method used to dry the glass fiber. At ordinary temperature glass may retain even in very dry air (over P_2O_5) a layer of water as thick at 10.55×10^{-6} mm., and at 107° C. up to 7.03×10^{-6} mm.

Thus it is easy to understand why pressure changes within one atmosphere show little or no effect upon the rate of formation of these thin films where the pressure amounts to hundreds of atmospheres. Likewise the solution of gases in these thin films under high pressure appears reasonable, as well as the long period of time necessary for the establishment of equilibrium.

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[a] Forsch. Geb. Agr.-Phys., **15**, 201 (1892).

[b] Ann. Phys. Chem., **14**, 450 (1881).

[c] Ann. Phys. Chem., **20**, 545 (1883); **22**, 145 (1884).

[d] Ann. Phys. Chem., **24**, 321 (1885).

Mülfarth[a] has investigated the adsorption of gases by glass powders, with the following results: (1) Perfectly dry glass powder adsorbs a considerable mass of carbon dioxide. This is contrary to the experimental results of Krause.[b] (2) Glass powder dried at 420° C. and rendered free from gas shows an adsorption of carbon dioxide as great as glass dried at 500°. (3) The adsorption of the CO_2 by completely dried glass powder is normal; that is to say, it increases with increasing pressure and decreases with increasing temperature. (4) The adsorption of carbon dioxide by dried glass powder is completed in a short time—from one to two hours. (5) The presence of moisture renders the adsorption of CO_2 slower; nevertheless, in a few days it proceeds to completion, and the mass adsorbed is not greatly different from that taken up by dried glass powder at the same pressure and temperature. Consequently, the main influence of dampness appears to consist in rendering the process of adsorption slower. (6) The quantity of carbon dioxide adsorbed is not nearly so great as Bunsen found in his research using glass fiber. (7) The adsorption of sulphur dioxide by dried glass powder proceeds exactly like that of carbon dioxide, is completed in two hours, increases with increasing pressure, and decreases with increasing temperature. (8) At zero degress the following gases are adsorbed by glass powder and in the following order: Ammonia, sulphur dioxide, carbon dioxide, nitrous oxide (N_2O), acetylene, in descending series. The gases, sulphur dioxide and ammonia, which are most easily condensed to liquid, are the most strongly adsorbed. Nitrous oxide and carbon dioxide, which stand very near to each other in respect to the ease of their condensation at low pressures, are almost equally well adsorbed, but carbon dioxide a little more strongly. (9) Henry's law holds fairly well also for the adsorption of gas on glass powder.

Absorption of ammonia.

Ammon[c] found that ammonia is absorbed by soil constituents as follows: Humus at 20° C., 11.5 per cent of its dry weight; ferric hydroxide, 4.7; quartz powder, 0.295; calcium carbonate, 0.23; kaolin, 0.42. When pure ammonia gas is absorbed, small quantities of nitric acid are formed, relatively more in ferric hydroxide than in the other soil constituents. The absorption of ammonia in general decreases with increase in temperature, but near zero, Centigrade, the maximum quantity of gas is taken up, less being absorbed at lower as well as at higher temperatures. In view of the more recent work by Dewar[d] and others on the absorption of gases at low temperatures the actual existence of such a maximum as Ammon found is open to question.

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[a] Ann. Phys. (4), **3**, 328 (1900).

[b] Ann. Phys. Chem., **36**, 923 (1889).

[c] Forsch. Agr.-Phys., **2**, 34 (1879).

[d] Chem. News, **94**, 174 (1906).

Von Dobeneck[a] has confirmed Ammon's conclusion that the absorption of ammonia is less the higher the temperature when working above zero, Centigrade. Von Dobeneck's quantitative measurements on the absorption of ammonia are in general of the same order of magnitude as those given by Ammon, and in addition von Dobeneck has shown that mixtures of soil constituents absorb ammonia and other gases additively, each material exerting its absorption effect independently of the others. He showed, too, that where a moist powder absorbs ammonia, the quantity of gas retained is very considerably in excess of what the water can dissolve when separate from the powder. Thus, 100 grams water dissolved 43.9 grams of ammonia, but when this same mass of water was held by 854 grams of kaolin, 56.5 grams of ammonia were absorbed, an increase of 28.6 per cent; with 472 grams kaolin and 100 grams water, 55.7 grams ammonia were absorbed. Similarly the following powdered solids, each wet with 100 grams water absorbed ammonia: 445 grams calcium carbonate, 54.6 grams; 435 grams quartz, 53.1 grams; 329 grams kaolin, 54.0 grams; 200 grams ferric hydroxide, 47.2 grams; 202 grams humus, 78.5 grams; 186 grams kaolin, 51.9 grams.

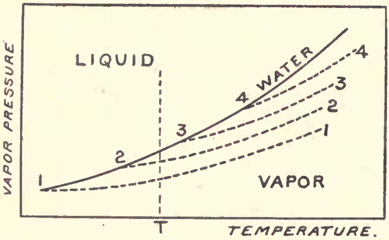

FIG. 9. Curves showing vapor pressure of water, and of moist soils at various temperatures for case I, assuming that absorption increases with rise in temperature.

Schlösing[b] found that soils, whether acid or alkaline, dry or wet, absorbed ammonia from the atmosphere in appreciable amount. Calcium carbonate in the soil increases the absorption capacity of the soil for ammonia. Absorption is in a high degree dependent upon a continual renewal of air at the surface of the soil, consequently, it makes a difference whether the surface be bare or covered with vegetation, since the plants tend to prevent circulation of the air in a layer near the surface.

Pfeiffer[c] showed that equal changes in pressure produce about equal changes in the quantity of gas absorbed by different sorts of carbon. He found that the absorption of ammonia by charcoal decreased about one-half on heating from 0° to 70° C.

Absorption of hydrogen.

The absorption of hydrogen is of minor importance from the standpoint of soil chemistry. Joulin[d] showed that ignited charcoal absorbs hydrogen so rapidly as to render difficult a measurement of the velocity, and recently Travers[a] has studied the absorption of hydrogen by cocoanut charcoal at different temperatures. The numerous investigations on the absorption of hydrogen by metals need only be mentioned in this connection.[b]

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[a] Forsch. Agr.-Phys., **15,** 201 (1892). [b] Compt. rend., **110,** 429, 99 (1890).

[c] Über die Verdichtung von Gasen durch feste Körper; Inaug. Diss. Erlangen (1882).

[d] Compt. rend., **90,** 741 (1880).

EFFECT OF TEMPERATURE UPON ABSORPTION.

THEORETICAL CONSIDERATIONS.

Assuming for the particular substance, water, that the quantity of moisture absorbed by a soil from a saturated atmosphere varies with the temperature, there are two possible cases:

(1) The amount of water absorbed increases with the rise in temperature. For this case the vapor-pressure-temperature curves for the soils will cut the vapor-pressure-temperature curve for water, as shown in figure 9; this has apparently been realized experimentally by Hilgard.[c]

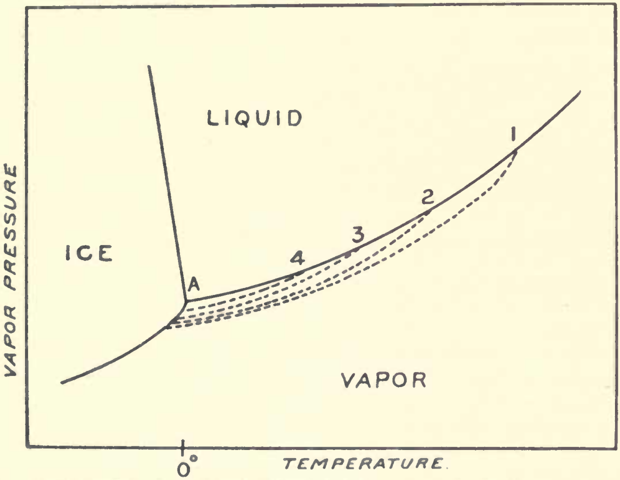

FIG. 10.—Curves showing vapor pressure of water, and of moist soils at various temperatures for case II, assuming that absorption decreases with rise in temperature.

(2) The amount of water absorbed from a saturated atmosphere decreases with rise in temperature. This case is illustrated by figure 10. Here the lower limit of the vapor-pressure curves for soils is the vapor-pressure-temperature curve for ice, and the maximum quantity of water absorbed at any temperature whatever is the mass of water which can remain adsorbed by the soil, in equilibrium with

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[a] Proc. Roy. Soc. London, 78, Ser. A, 9–22 (1906).

[b] See Fischer, Ann. Phys. (4), 20, 503 (1906).

[c] "Soils," pp. 196, 198 (1906).

the complete system—ice, "liquid water," water vapor, which exists at the triple point A. The dotted curves in figure 10 show the vapor-pressure-temperature curves for soils. The quantity of moisture in the soil remains constant along the dotted curve, which is limited in extent; above, it meets the vapor-pressure curve of liquid water; below, it cuts the vapor-pressure curve for ice. Here the absorbed water would begin to freeze at a lower temperature than free water; and when we remember the enormous stress under which water exists when in adsorbed condition, this conclusion is not surprising.

EXPERIMENTAL DATA AND DISCUSSION.

Four series of preliminary experiments were carried out. In the first three series 10-gram samples of dry quartz flour, Podunk fine sandy loam, and Sea Island cotton soil were brought to equilibrium with water vapor in desiccators at various temperatures in the thermostat. The general trend of these results serves very well to show that the mass of water vapor absorbed decreases with the temperature. And by comparison of this series for Sea Island cotton with a later series for the same soil under rigid conditions, using stoppered weighing bottles to avoid loss of moisture on the balance, the exact experimental error is seen at each point.

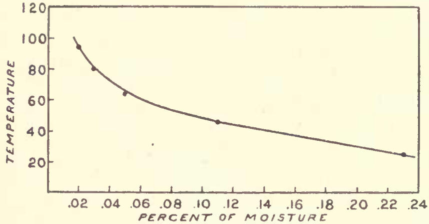

FIG. 11.—Curve showing decrease in absorption of water vapor by quartz flour with rise in temperature.

The results for quartz flour given in Table XIII and plotted in figure 11 show a decrease of 91 per cent in the water absorbed for an increase of 74° C.

TABLE XIII.—*Decrease of absorption with temperature rise for quartz flour*[a] *in open dish over water.*

Temperature.	Water held by soil.
°*C.*	*Per cent.*
23	0.23
43	.11
62	.05
80	.03
97	.02

[a] The same sample was used throughout.

TABLE XIV.—*Decrease of absorption with temperature rise for Podunk soil in open dish over water.*

Temperature.	Water held by soil.
°C.	*Per cent.*
25	0.81
43	.35
62	.16
80	.11

TABLE XV.—*Decrease of absorption with temperature rise for Sea Island cotton soil in open dish over water.*

Temperature.	Water held by soil.
°C.	*Per cent.*
25	8.4
62	4.84
80	3.84

TABLE XVI.—*Decrease of absorption with temperature rise for Sea Island cotton soil in weighing bottles over water.*

Temperature.	Water held by soil.
°C.	*Per cent.*
25	9.7
100	5.5 5.4

Podunk fine sandy loam confirms the general trend shown by quartz, as seen in Table XIV and figure 12. The soil absorbs over 50 per cent less water vapor at 43° than at 25°, and a rise in temperature of only 55°, from 25° to 80°, reduces the moisture content at equilibrium by 86 per cent. Sea Island soil in open dishes over water shows in Table XV a decrease in absorption of 42 per cent for a rise of 32°, and of 54.2 per cent for 55°.

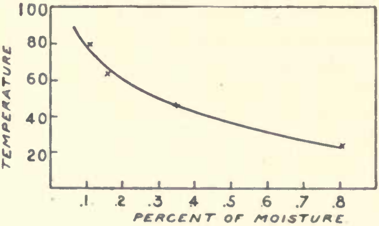

FIG. 12.—Curve showing decrease in absorption of water vapor by Podunk soil with rise in temperature.

A fourth series for Sea Island cotton soil is given in Table XVI. The quantity of water absorbed at 25° over water in a desiccator was determined, using a 20-gram sample in a weighing bottle which could be closed during the weighing to avoid evaporation. The data for this point are taken from the lower half of Table IV and were obtained under accurately controlled temperature conditions; the equilibrium conditions were established after a run of ninety-seven days.

The absorption at 100° C. was found by inclosing the weighing bottle with its 20-gram soil sample in a sealed tube over water. This tube was immersed in boiling water, as shown in figure 13, where T is the sealed tube; W, the weighing bottle; S, a copper support to hold the bottle out of the water; G, a safety guard of gauze surrounding the tube T and also serving as a support; C, a cork support for T and G; H, hooks holding the gauze G to the cork C; B_1, a beaker containing boiling water nearly to the level of the cork C; B_2, a tall beaker inverted over B_1 and serving as a condenser.

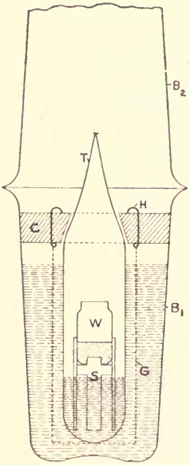

FIG. 13.—Diagram of apparatus used to determine absorption of water vapor by soil at the boiling point of water.

With this arrangement water need be added to B_1 only every two days. On account of the high temperature, absorption proceeded rapidly to completion; equilibrium was established within a week, as shown by the values given in Table XVI. After one week 5.5 per cent of moisture had been absorbed, and another week's run gave practically the same value, 5.4 per cent; so the system had come to equilibrium. The difficulty met with in the other experiments, Tables XIII, XIV, and XV, did not enter here, since a closed weighing bottle was used.

The data for the two points in Table XVI are shown in figure 14 as curve 1, and for comparison the data from Table XV are given on the same plot and to the same scale, with temperature as ordinate and percentage moisture in the soil as abscissa. It is evident that the determinations made in open dishes, curve 2, show less moisture than those made in weighing bottles, curve 1. At 80° C. this loss of absorbed moisture from an open evaporating dish during weighing amounts to nearly 40 per cent, at 25° C. this loss is 13 per cent, and for 100° C. extrapolation of curve 2 indicates a loss of some 48 per cent of the total. The curves in figs. 11,

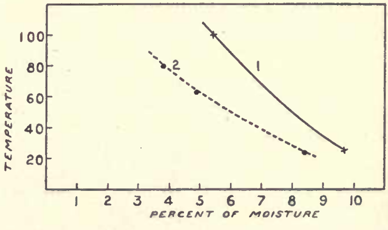

FIG. 14.—Curve showing decrease of absorption of water vapor by Sea Island cotton soil with rise of temperature.

2, and 14 show the same general trend, and together with the most accurately determined points in Table XVI and curve 1, figure 14, show a decrease of absorption as temperature rises in a manner not open to question. All of these curves bend upward steeply at higher temperatures, since the absorbed moisture is held more firmly the thinner the layer in which it is spread upon the soil grains.

Thus it is proved experimentally that absorption of water vapor by soils decreases very greatly with rise in temperature. A departure from equilibrium conditions, which indeed seldom obtain in the field, shows even greater decrease in the quantity of absorbed water as the temperature increases.

ABSORPTION CAPACITY.

It is of interest to see how the absorption data are related to the surface presented by the grains of the different soils used. For this purpose a general survey of the quantity of vapors absorbed by some of the soils studied in the foregoing sections is given in Table XVII.

Unfortunately the area of a soil as calculated from its mechanical analysis (Table XVIII) can give only an approximate result, probably much below the true value. Thus in Table XVII it is seen that Galveston clay absorbs three times the mass of water vapor that Marshall silt loam takes up, while the calculated area of the clay is not three times as great but less than a third greater than the silt loam. The results obtained with toluene were in general similar to those obtained with water. The ether vapor behaves differently, the clay taking in a smaller quantity than would be predicted from the water and toluene results.

Table XIX contains the calculated thickness of the layer of liquid absorbed upon the grains of each soil. The following assumptions were made in deriving these values: (1) That the film of absorbed vapor is uniform in thickness over all the soil grains; (2) density of water, 1; density of toluene, 0.89; density of ether, 0.73; as these densities are probably lower than the density of the surface film the value for the thickness of film is probably too high; (3) density of individual soil grains, 2.5; (4) that the soil grains are spheres; this assumption probably gives a value of the film thickness much too high; (5) that the fractions in the mechanical analyses are clean separations. In the last two fractions the diameters of the grains vary within relatively wide limits. The area of the soil grains is probably several times greater than the value given in Table XVII. For example, the quantity of water absorbed by Galveston clay is much greater than would be expected from its area when the absorption capacity of the other soils and their areas are considered. The clay and silt in the Galveston clay greatly increase its surface beyond that calculable from a mechanical analysis. It was on this account that the soil separate with grains varying only between 0.1 and 0.05 mm. in diameter was used in this series, so that a more accurately determined surface might be used for the determination of its absorption capacity.

TABLE XVII.—*Area of soil grains as related to absorption capacity for vapors.*

Soil.	Area per gram.	Water absorbed.		Ether absorbed.		Toluene absorbed.	
		Eight days.	Maximum.	Eight days.	Maximum.	Eight days.	Maximum.
	Sq. cm.	*Per ct.*	*Per cent.*	*Per ct.*	*Per cent.*	*Per ct.*	*Per cent.*
Galveston clay	3,280	8.00	12.00	4.80	6.00	4.79	....
Marshall silt loam	2,320	2.84	4.00	2.86	4.00	1.62	1.7
Hagerstown loam	2,270	2.90	4.50	3.30	4.50	1.85	....
Quartz flour	1,260	.35	.80	....	....	.29	.4
Soil separate (0.1-0.05)	320	.67	1.00	.77	.77	.41	....
Norfolk sand	300	.29	.45	.45	.62	.17	....

TABLE XVIII.—*Mechanical analyses.*

Soil.	Average diameter of grain.						
	2-1 mm.	1-0.5 mm.	0.5-0.25 mm.	0.25-0.1 mm.	0.1-0.05 mm.	0.05-0.005 mm.	0.005-0 mm.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Galveston clay	0.7	1.5	0.40	7.0	28.9	30.1	31.00
Hagerstown loam	.9	3.0	2.10	6.5	13.9	54.3	19.10
Marshall silt loam	1.3	2.8	1.70	4.3	12.9	56.9	19.50
Quartz flour	.0	.0	.05	.2	8.0	86.2	5.42
Norfolk sand	.2	6.3	22.20	63.7	4.1	1.0	1.80

TABLE XIX.—*Comparison of absorption capacity of soils for vapors.*

Soil.	Vapor.	Total quantity absorbed.	Quantity per sq. cm. × 10^5.	Thickness of layer.	Energy = latent heat × grams absorbed.
		Grams.	*Grams.*	*Cm.* × 10^5.	
Soil separate (0.1-0.05). 8 days absorption.	Water	0.6417	2.00	2.00	378.2
	Toluene	.4049	1.26	1.42	33.8
	Ether	.770	2.40	3.25	65.8
Galveston clay, maximum absorption	Water	12.00	3.66	3.66	7,080.0
	Toluene	6.00	1.83	2.06	501.0
	Ether	6.00	1.83	2.51	518.0
Marshall silt loam	Water	4.00	1.72	1.72	2,360.0
	Toluene	1.70	.73	.82	240.0
	Ether	4.00	1.72	2.35	345.0
Hagerstown loam	Water	4.50	1.98	1.98	2,655.0
	Toluene	1.85	.82	.92	155.0
	Ether	4.00	1.68	2.31	345.0
Norfolk sand	Water	.45	1.50	1.50	265.5
	Toluene	.25	.83	.94	20.9
	Ether	.62	2.06	2.83	53.5
Quartz flour	Water	.80	.64	.64	471.0
	Toluene	.40	.32	.36	334.0

TABLE XIX.—*Comparison of absorption capacity of soils for vapors*—Continued.

Soil.	Vapor.	Vapor pressure.	Temperature.	Surface tension.	Viscosity.	Density.
		Mm.	°*C.*	*C. G. S.*	*C. G. S.*	*C. G. S.*
Soil separate (0.1-0.05), 8 days absorption.	Water	28.1	28	73	0.01	1.00
	Toluene	33.5	28	28	.0056	.89
	Ether	575.0	28	17	.0024	.73
Galveston clay, maximum absorption.	Water	28.1				
	Toluene	33.5				
	Ether	575.0				
Marshall silt loam	Water	28.1				
	Toluene	33.5				
	Ether	575.0				
Hagerstown loam	Water	28.1				
	Toluene	33.5				
	Ether	575.0				
Norfolk sand	Water	28.1				
	Toluene	33.5				
	Ether	575.0				
Quartz flour	Water	28.1				
	Toluene	33.5				

This soil separate shows a film 2.0×10^{-5} cm. thick, as against a thickness of 3.66×10^{-5} cm. for Galveston clay and 1.5×10^{-5} for Norfolk sand, while Hagerstown loam and Marshall silt loam give values nearer that of the soil separate. Parks[a] gives a value for the thickness of a water film absorbed on glass wool, 1.34×10^{-5} cm., which agrees closely with these results.

In general, toluene gives a thinner film than water, while the ether layer is thicker than that of water for all soils save Galveston clay.

If we assume the average diameter of a clay particle as 0.0002 cm., and consider it to be a sphere, its volume is 4.19×10^{-12} c. c. If the water film be uniform in thickness over the surface of all the grains, 2.00×10^{-5} cm., as given for the soil separate, then the total volume of this clay particle with its absorbed water will be 7.25×10^{-12} c. c., and the volume of water alone 3.06×10^{-12} c. c., or 73 per cent of the volume of the clay particle holding it, and the radius of the particle is only ten times greater than the thickness of the water layer surrounding it. There is very little doubt that this hygroscopic water is in part held in the fine capillary spaces between the soil grains,[b] but we have no sharp experimental method of ascertaining what fraction of the water is thus retained.

A comparison of the quantities of water, toluene, and ether absorbed by the various soils, with their surface tensions, viscosities, vapor pressures, and latent heats of evaporation does not give a clue to the different absorption capacities found. It seems that each vapor has its own specific action which finds a counterpart in the selective absorption exercised by the soil. For any one vapor the absorption capacity of a soil is roughly proportional to the soil grain surface as calculated from the mechanical analysis.

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[a] Loc. cit.

[b] Katao, Über die Wasserbewegung in Boden, Bul. Col. Agr., Imp. Univ., Tokyo, Vol. 3, No. 1, 1897; Soyaka, Forsch. Agr. Phys. **8**, 1 (1885); Whitney, Agricultural Science, Vol. 3, p. 199, 1889; Briggs, Bul. No. 10, U. S. Dept. of Agriculture, Division of Soils (1897).

Finally, we see from the above considerations that for any one vapor the amount of absorption is proportional to the calculated soil area exposed, and that the thickness of film on any given soil surface varies with the nature of the vapor, but the data at present available are not sufficient to show that the thickness of the film is dependent upon the nature of the soil type.

DISTRIBUTION.

Solids in general do not completely absorb gases or vapors, but rather the gas is divided between the atmosphere and the solid. The greater the quantity of gas or vapor in the atmosphere, the more of it is held fixed by the solid, until the solid becomes saturated and can retain no more of the gas. A number of attempts have been made to express this relation between the quantity absorbed by the solid and the concentration of gas in the atmosphere, as a fairly simple mathematical equation. The chemical composition of the solid and that of the gas of course determine in great measure the degree to which absorption takes place, and this factor is expressed by a constant which is different for each solid and gas studied. The effect of temperature upon absorption is likewise recognized in the formula by a constant whose value changes with the temperature.

De Saussure[a] has suggested the formula $V = 19.1 + 0.53\ P$, where V is the volume of gas adsorbed and P is the pressure in inches of mercury. This relation holds for carbon dioxide.

Ostwald[b] applies to gaseous adsorption the equation, $\frac{x}{m} = \alpha C^{\frac{1}{p}}$, which was developed for adsorption from solution, where x is the mass of gas adsorbed; m the mass of adsorbent solid; C the concentration of the vapor phase; α is a constant; and $\frac{1}{p}$ is an exponent. Freundlich holds that adsorption from solution and from vapor by solids follow the same law, and Ostwald's exponent, $\frac{1}{p}$ equals $1 - \frac{1}{n}$, where $\frac{1}{n}$ is the exponent in the equation,[c] $\lambda = \alpha\left(\frac{a}{v}\right)^{-\frac{1}{n}}$, proposed by himself.

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[a] Loc. cit.

[b] Lehrbuch der Allgemeine Chemie, II (2 Aufl.) 232.

[c] $\lambda = \alpha\left(\frac{a}{v}\right)^{-\frac{1}{n}}$ is simply an empirical relation, and is not derived analytically from the other equation, $\lambda = \frac{v}{m} \ln\left(\frac{a}{a-x}\right)$ given by Freundlich. λ and α are constants; a is total mass of gas in the system, and v is the volume of space available for the gas.

Thus Freundlich found working with liquid solutions, values for $\frac{1}{n}$, which range from 0.86 to 0.485, giving to $\frac{1}{p}\left(=1-\frac{1}{n}\right)$ values from 0.14 to 0.515. But the $\frac{1}{p}$ given by Ostwald on the basis of Chappuis,[a] Joulin,[b] and Kayser's [c] results, for CO_2 adsorbed by various kinds of charcoal, is higher, varying from 0.50 to 0.75. Further, Chappuis's curve for log $\frac{x}{m}$ against C is very concave for carbon dioxide, whereas if the exponential formula $\frac{x}{m}=\alpha C^{\frac{1}{p}}$ applies, this curve should be a straight line. So this formula of Ostwald's holds only indifferently well as far as this gas is concerned.

Recently Travers[d] has determined the distribution of hydrogen and of carbon dioxide between cocoanut charcoal and the vapor at 100°, 60°, 35°, 0° and – 78°, and for hydrogen at – 190° C. He suggests the formula, $\sqrt[n]{\frac{p}{x}}$ = a constant, where P is the gas pressure and x the concentration of the gas, in the solid phase for each temperature. The value of n increases when the temperature falls. For CO_2 at 0°, $n=3$; at 100°, $n=2$; at higher temperatures n would probably equal 1 and then the distribution law would hold exactly—i. e., become linear—but it is possible, too, that n might fall below 1. Hydrogen at – 190° behaves exactly like CO_2 at 0°; that is, $n=3$. Travers attributes the departure of the distribution law from a linear form at low temperatures to the influence of diffusion into the solid phase. On the contrary, Trouton[e] has assumed the formation of a liquid phase upon the surface of the solid to explain his curves representing the absorption of water vapor by cotton.

It is seen that no one mathematical expression yet proposed describes the present data for the adsorption of gases by solids. The specific attractions of solid and gas, the diffusion of gas into solid, the condensation of gas to liquid, and the consequent clogging of capillary channels where the forms and arrangement of these minute spaces enter to determine the vapor pressure of the liquid there enmeshed, all these factors complicate the observed relation of mass of gas adsorbed to mass of gas left in the vapor phase.

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[a] Ann. Phys. Chem., **12**, 161 (1881).

[b] Ann. Chim. Phys. (5), **22**, 397 (1881).

[c] Ann. Phys. Chem., **12**, 526 (1881).

[d] Proc. Roy. Soc. London, **78**, Ser. A, 9 (1906).

[e] Proc. Roy. Soc. London, **77**, Ser. A, 292 (1906).

RATE OF ABSORPTION.

DETERMINING FACTORS.

The rate at which a solid absorbs a vapor depends upon several factors. These will be discussed in the following paragraphs.

Chemical composition.

In general, the chemical composition of the solid affects absorption to the extent that acid bodies tend to absorb basic vapors, and conversely. The magnitude of this influence varies from very pronounced chemical reaction, such as the fixation of gaseous ammonia by solid acids to extremely weak acid or basic effects.

Physical condition.

The physical condition of the solid, its fineness of division, determines the surface available for the purely adsorption effect, which, with other conditions the same, is directly proportioned to the surface of the solid in contact with the vapor. As the solid is reduced to finer powder the number of solid angles between the granules is increased, as well as the surface of solid exposed, and the condensed vapor retained in these solid angles is added to that held by simple absorption.

Viscosity of the vapor.

In the case of vapor entering a soil at rest there is a damping term due to the viscosity of the vapor. After taking account of the probable diameter of the capillary spaces through which the vapor is to pass, the resistance which the vapor offers to being forced into the soil is the viscosity of the vapor multiplied by its rate of flow,[a] and this rate of flow is the rate at which absorption is taking place. The diameters of the capillary spaces, too, become less as the surface of each grain takes on moisture, so the resistance to the passage of vapor increases as the absorption proceeds. Consequently we should expect rate curves for soils to show a decrease in rate of absorption with time greater than that for absorption of vapor upon a plane surface, but this factor has been found to be of only minor import.

Absorption capacity.

The absorption capacity of the solid affects the rate of absorption to a marked degree. Where the absorption capacity is high, the speed of absorption is very great.

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[a] See E. Wollny, Forsch. Agr.-Phys. **16**, 193 (1893); Buckingham, Bul. No. 25, Bureau of Soils, U. S. Dept. Agr. (1904).

Partial pressure, or humidity.

The rate of absorption of water by soils varies for atmospheres of different humidity in a manner similar to the change in rate of evaporation under different degrees of humidity, as can be seen from the curves in figure 15 for Sea Island cotton soil plotted from the data given in the lower half of Table IV. Ordinates are in percentage of moisture in the soil, abscissas are in time in days. All the experiments begin at 4.4 per cent of moisture, the quantity retained by Sea Island cotton soil in air-dry condition.

Van Bemmelen,[a] Hellriegel,[b] Puchner,[c] and von Dobeneck [d] have determined the speed with which a soil absorbs water vapor.

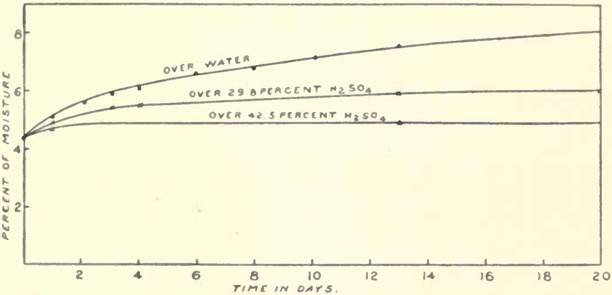

Fig. 15.—Curves showing rate of absorption of water vapor by Sea Island cotton soil under different degrees of humidity.

They, too, give very regular rate curves, but these, as well as Parks[e] rate of absorption of water vapor by glass wool, are likewise not described by a simple mathematical formula. Hantzsch[f] has shown that the rate of absorption of ammonia gas by solid organic acids in finely powdered condition depends upon the partial pressure of the ammonia gas in the atmosphere above the solid acid. Using absolute ammonia, the reaction is fairly well described by the first order reaction velocity equation, $K^{I.} = \frac{1}{t} \log.\left(\frac{a}{a-x}\right)$, and on dilution of the ammonia with air, this equation still holds if the total volume of gas employed is so great that the partial pressure of the ammonia is practically constant throughout the absorption process.

If, however, the quantity of ammonia present in the gas is considerably reduced by the absorption, then the rate of absorption is no longer expressed by this first order reaction velocity equation, but is more nearly given by the second order equation, $K^{II.} = \frac{1}{t} \frac{x}{(a-x)a}$. The same is true for the absorption of gaseous hydrogen chloride by solid organic bases. A similar effect is produced in the rate of absorption of water vapor by a soil as the atmospheric humidity varies.

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[a] Arch. Néer. (2), **10**, 267 (1906).

[b] Forsch. Agr.-Phys. **6**, 389 (1883).

[c] Land. Vers.-Stat., **46**, 229 (1895).

[d] Forsch. Agr.-Phys., **15**, 163 (1892).

[e] Phil. Mag. (6), **5**, 518 (1903).

[f] Zeit. phys. Chem., **48**, 289 (1904).

The rates of absorption of water vapor by humus from atmospheres saturated at different temperatures, as determined by von Dobeneck (Table XX), show, too, that the velocity of absorption is greater the higher the relative humidity.

The rate curves obtained from all of the foregoing tables are regular, but are not described by a simple velocity equation.

TABLE XX.—*Rate of absorption of water vapor by humus, according to von Dobeneck.*

Period.	Quantity of water absorbed at—						
	[a] 0° C.	[a] 10° C.	[a] 20° C.	[a] 30° C.	[b] 10° C.	[b] 20° C.	[b] 30° C.
Days.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
1	0.12	1.40	1.96	3.59	1.35	1.61	2.14
2	.50	2.47	3.22	6.27	2.22	2.48	2.29
3	.88	3.61	4.84	8.13	3.24	2.99	2.32
4	1.25	4.57	5.77	10.03	4.37	3.47	2.36
5	1.79	5.44	7.11	11.17	5.28	3.63	2.39
6	2.28	6.19	8.33	12.39	6.17	3.77	2.43
7	2.79	7.01	9.36	13.61	6.76	3.92	2.42
8	3.30	8.11	10.18	14.20	7.28	4.01	2.45
9	3.76	8.76	10.88	14.65	7.61	4.08	2.49
10	4.23	9.34	11.39	15.34	7.91	4.13	2.48
12	5.06	9.65	12.51	15.98	8.32	4.15	....
14	5.95	10.37	13.32	....	8.49	....	....
16	6.89	11.13	14.03	....	8.60	....	....
18	7.60	12.02	14.64	....	8.63	....	....
20	8.32	12.83	15.02	....	....	....	....
22	9.09	13.62	15.28	....	....	....	....
24	9.90	14.20	15.56	....	....	....	....
26	10.61	14.70	15.86	....	....	....	....
28	11.22	15.03	15.89	....	....	....	....
30	11.83	15.38	....	....	....	....	....
32	12.43	15.68	....	....	....	....	....
34	12.96	15.95	....	....	....	....	....
36	13.48	....	....	....	....	....	....
38	13.99	....	....	....	....	....	....
40	14.46	....	....	....	....	....	....
42	14.89	....	....	....	....	....	....
44	15.25	....	....	....	....	....	....
46	15.59	....	....	....	....	....	....
48	15.79	....	....	....	....	....	....
50	15.90	....	....	....	....	....	....

[a] Atmosphere saturated with moisture at temperature given.
[b] Atmosphere saturated with moisture at 0°.

Previously absorbed vapor.

As will be seen from the data on the rate of absorption of vapors by soils in Tables II, III, IV, V, VI, VIII, IX, X, and XI, the rate of absorption decreases as more and more vapor is held by the soil. This effect is only what would be expected when we remember that the last portions of vapor absorbed and condensed to liquid form exist to a considerable extent in the capillary spaces of the soil as well as in the form of films upon the surface of the soil grains.

Temperature.

(*a*) It has been shown by the investigations cited above and by the new experiments given in the section on the effect of temperature upon absorption, that in saturated atmospheres, at least, an increase in temperature decreases the mass of vapor absorbed by a solid. (*b*) Increase in temperature increases the mass of vapor which a given volume of air can hold at any one pressure. Theoretically, then, the first temperature effect (*a*) should reduce the time required to saturate the absorbing solid with vapor; and the second effect (*b*) should likewise hasten the absorption by providing a higher absolute quantity of vapor in the atmosphere for the solid to draw upon. This conclusion is borne out experimentally by the results obtained with Sea Island cotton soil; at 100° C. only one week was required for this soil to absorb all the vapor it could take up, whereas at 25° C. this same soil stood ninety-seven days over water before it ceased to absorb moisture. Von Dobeneck[a] confirms this effect of temperature upon rate of absorption as shown in Tables VII and XX.

Joulin[b] found that the time required to saturate charcoal with carbon dioxide decreased with increasing temperature at a constant pressure.

RATE OF EVAPORATION.

In a former bulletin the mechanism of evaporation has been discussed in considerable detail.[c] In addition to the data on the evaporation of moisture from soils under various degrees of humidity, which have been given in Tables II, III, and IV, above, we repeat here in Tables XXI, XXII, XXIII, and XXIV the data in that bulletin on the rate of evaporation from wet soils over concentrated sulphuric acid at 25° C. The point brought out by the evaporation data in all of these tables is that the rate of evaporation from any wet soil is fairly constant until the quantity of moisture still remaining in the soil is approximately that known as the "optimum water content" of the soil. At this point a gradual change in the rate of evaporation takes place, as shown in figures 16, 17, 18, and 19, which represent graphically the rate of evaporation indicated in Tables XXI, XXII, XXIII, and XXIV. Referring back to figures 1, 2,

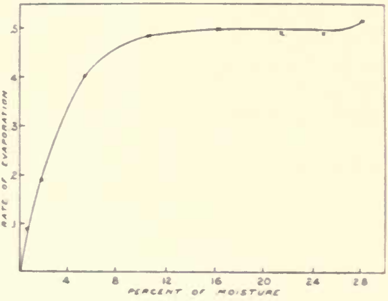

FIG. 16. Curve showing rate of evaporation of water from Podunk soil.

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[a] Loc. cit.

[b] Comp. rend., **90**, 741 (1880).

[c] Cameron and Gallagher, Bul. 50, Bureau of Soils, U. S. Dept. Agr., 1907.

and 3 we see this same bend in the rate of evaporation curves, which becomes less and less evident as the humidity of the atmosphere of the soil approaches the saturation point, going from the partial pressure of water vapor of 94 per cent sulphuric acid up to that of the vapor pressure of water alone. As was stated in Bulletin 50, the moisture content of each of these soils at which this bend in the rate of evaporation takes place is in reality very close to the content of water in the soil which gives it the best physical condition for plant growth. The reason for this agreement between the point at which the rate of evaporation changes and the point known as the "optimum water content" has been also pointed out in Bulletin 50. The larger open spaces between the soil grains naturally lose their water first, and the later portions of water evaporate more and more from the finer capillary spaces in the soil. When the water content of the soil is reduced to such a degree that the loosely held water in these more open spaces must draw upon the water held as a capillary film upon the soil grains, then very naturally evaporation proceeds more slowly, since the films are held by the soil grains quite tenaciously. At this same moisture content, too, where the pull of the capillary films of water upon the soil grains is brought into evidence, we would naturally expect that the very fine soil particles might be rearranged into larger aggregates and thus furnish a more open structure better suited for access of atmospheric gases and for the penetration of roots.

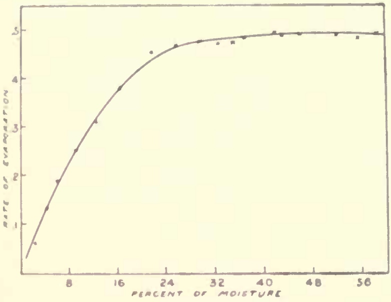

FIG. 17.—Curve showing rate of evaporation of water from Miami soil.

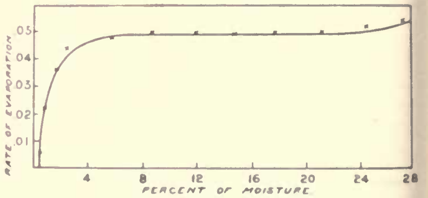

FIG. 18.—Curve showing rate of evaporation of water from Leonardtown soil.

In this connection it is interesting to note that Heinrich[a] has shown that the quantity of water in a soil required for plant growth is always greater than the quantity of water the soil can take up from a saturated atmosphere. A heavy soil containing a high percentage of moisture may hold the water so absorbed that while the plant can get some water, still it is by no means fully supplied.

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[a] Zweiter Ber. landw. Vers.-Stat. Rostock, p. 19 (1894): E. S. R., **7**, 481 (1895–96). See also Spalding, Bot. Gaz. **38**, 122 (1904).

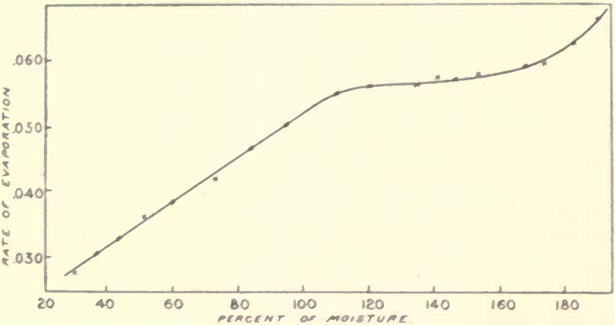

FIG. 19.—Curve showing rate of evaporation of water from muck soil.

TABLE XXI.—*Rate of evaporation from Podunk fine sandy loam over 95 per cent sulphuric acid at 25° C., according to Cameron and Gallagher.*

Mean moisture content.	Period.	Loss of moisture.	Loss per hour.
Per cent.	*Hours.*	*Grams.*	*Grams.*
27.4	19.5	1.0450	0.0563
24.2	4.5	.2812	.0625
21.3	18.7	.9210	.0493
17.8	9.3	.4595	.0494
14.8	15.3	.7495	.0490
12.0	9.9	.4854	.0490
8.7	14.5	.7140	.0492
5.8	9.9	.4712	.0476
2.4	4.0	.1732	.0433
1.7	2.0	.0719	.0359
0.9	11.0	.2445	.0222
0.3	2.0	.0097	.0049

TABLE XXII.—*Rate of evaporation from Miami black loam over 95 per cent sulphuric acid at 25° C., according to Cameron and Gallagher.*

Mean moisture content.	Period.	Loss of moisture.	Loss per hour.
Per cent.	*Hours.*	*Grams.*	*Grams.*
58.5	16.70	0.8198	0.0491
55.4	9.30	.4474	.0481
52.4	15.17	.7422	.0489
49.4	9.90	.4802	.0485
46.4	14.50	.7155	.0493
43.4	9.90	.4808	.0486
41.0	11.00	.5427	.0492
37.5	11.00	.5411	.0483
35.4	6.50	.3099	.0477
32.6	17.50	.8296	.0474
29.7	7.00	.3321	.0474
25.9	17.00	.7964	.0468
22.1	24.00	1.0879	.0453
17.1	24.00	.9109	.0379
12.9	26.25	.8108	.0309
9.5	22.25	.5716	.0257
6.7	24.50	.4694	.0192
5.1	22.75	.3056	.0134
3.7	23.75	.2136	.0090
2.7	24.25	.1470	.0061

TABLE XXIII.—*Rate of evaporation from Leonardtown loam over 95 per cent sulphuric acid at 25° C., according to Cameron and Gallagher.*

Mean moisture content.	Period.	Loss of moisture.	Loss per hour.
Per cent.	*Hours.*	*Grams.*	*Grams.*
28.2	19.00	0.9770	0.0517
24.9	7.25	.3555	.0490
21.6	19.25	.9538	.0495
16.4	22.00	1.0962	.0498
10.7	24.50	1.1963	.0488
5.5	22.75	.9193	.0404
2.0	24.25	.4560	.0188
.7	24.16	.0904	.0037

TABLE XXIV.—*Rate of evaporation from muck over 95 per cent sulphuric acid, at 25° C., according to Cameron and Gallagher.*

Mean moisture content.	Period.	Loss of moisture.	Loss per hour.
Per cent.	*Hours.*	*Grams.*	*Grams.*
190	9.50	0.6362	0.0669
183	15.20	.9590	.0632
174	9.85	.5905	.0600
168	14.50	.8639	.0596
154	10.00	.5813	.0581
147	13.00	.7474	.0575
141	6.50	.3744	.0576
135	17.50	.9893	.0566
121	17.00	.9591	.0564
110	24.00	1.3233	.0551
95	24.00	1.2120	.0505
84	26.30	1.2332	.0469
74	22.10	.9329	.0423
60	24.30	.9388	.0387
52	23.00	.8352	.0363
44	24.00	.7958	.0331
37	24.00	.7372	.0307
30	24.50	.6851	.0279

ENERGY CHANGES.

Poggendorff attributes the first experimental work on capillarity to Leonardo da Vinci, 1452–1519. A number of investigators[a] worked in the field before it was discovered that capillary phenomena are accompanied by heat effects. De Saussure[b] during 1812 to 1814 found that heat was evolved during the process of absorption.

Pouillet[c] showed the rise in temperature of various powders and porous substances when moistened with a liquid. Unfortunately, he, as well as several investigators following him, neglected to communicate the weight of powder and of liquid used and their specific heats; so we are unable to calculate the quantity of heat set free. He gives merely the rise in temperature produced by adding liquid to the material, using water, oil, alcohol, and ethyl acetate with finely divided metals, metallic oxides, powdered glass, clay, and other substances, including a number of organic solids. Water added to inorganic solids gave a rise of 0.2° to 0.6° C., while with dried organic material the temperature rise sometimes reached 10° C.

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[a] Ann. Phys. (Gilbert's), **47**, 113 (1814).

[b] For a more extended survey of the literature see Trans. Am. Electrochem. Soc., **11**, 387 (1907).

[c] Ann. Chim. Phys., **20**, 141 (1822); Ann. Phys., **73**, 356 (1823).

Ammon[a] cites the observations of Von Babo[b] on the rise in temperature experienced by dry soils when subjected to an atmosphere saturated with water vapor. These experiments are qualitative only, but they show the existence of the heat effect due to moistening a powder; that it is positive, and that the temperature rise is greater with soils containing humus than without.

Stellwagg[c] found a marked increase in the temperature on moistening various soils and soil constituents with water and on subjecting them to humid atmospheres. But he has given no data enabling us to calculate the number of calories liberated during this adsorption; consequently his data have only qualitative value. He concludes: (1) That the rise in temperature which the soil experiences upon addition of water, in general is greater the drier the soil, the finer its grains, and the lower the prevailing temperature. (2) That the rise of soil temperature on addition of water to a perfectly dry soil is very considerable (8.33° C. for a calcareous sand rich in humus, 6.6° C. for ferric hydroxide, 5.57° C. for a loam soil). (3) That when water vapor is adsorbed by soil constituents a temperature rise is observed as follows: Quartz sand, 0.00–0.25 mm. diameter, 0.88°; quartz powder, 1.08°; precipitated calcium carbonate, 1.47°; kaolin, 2.63°; ferric hydroxide, 9.30°; peat, 12.25° C. (4) That the temperature rise due to adsorption of dry carbon dioxide by dry soil constituents is inconsiderable, with the exception of ferric hydroxide, in which case the rise is 6.9° C., while the moist gas is adsorbed with a much greater temperature increase. (5) That dry soil constituents adsorb dry ammonia and experience a considerable temperature rise: Quartz powder, 0.80°; precipitated calcium carbonate, 0.80°; kaolin, 2.05°; ferric hydroxide, 18.05°; peat, 28.3° C. Moist ammonia shows less temperature rise; for ferric hydroxide and for peat it is, respectively, 14.1° and 23.80° C.

This heat evolved when a vapor condenses upon a solid absorbent was very naturally attributed to the latent heat of vaporization which became available on liquefaction. But Favre[d] found the heat liberated by absorption to be greatly in excess of the latent heat of vaporization, for three different gases; consequently, this assumption had to be abandoned. More recently Dewar[e] has shown that hydrogen, whose latent heat of vaporization at its boiling point is 120 gram calories, gives off six times that quantity of heat when absorbed by charcoal at the boiling point of air. Similarly, oxygen gas when absorbed by charcoal liberates twice the heat due to liquefaction.

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[a] Forsch. Agr.-Phys., **2**, 21 (1879).

[b] Mülder, Chemie der Ackerkrume, Band 3, p. 366.

[c] Forsch. Agr.-Phys., **5**, 211 (1882).

[d] Lehmann, Molecular-Physik. I, p. 85.

[e] Chem. News, **94**, 174 (1906); Proc. Roy. Soc., **74**, 130 (1904).

The experiments of Parks[a] indicate that the quantity of water absorbed by a powder from water vapor is very nearly the same as the quantity of water held on the surface of the grains when the powder is immersed in liquid water. He has shown that a silica powder saturated with water vapor gives off no measurable heat when brought into contact with liquid water, whereas the dry silica liberates a definite quantity of heat per square centimeter of surface, and this heat evolution decreases in a perfectly regular manner as the silica powder contains more and more absorbed water vapor.

Masson[b] has shown that the heat evolved when cotton absorbs water vapor is for practical purposes directly proportional to the quantity of moisture absorbed and is very nearly the same as the latent heat of vaporization. He finds the absorption by cotton to be much greater than is warranted by its area as compared with similar experiments using glass wool, and suggests as an explanation that the water absorbed penetrates into the cotton fiber as a solid solution. The thermal effect dealt with here is evidently different from that studied by Parks.[c]

When a gas is absorbed by a metal many interesting physical changes in the metal may be effected. Its volume, hardness, elasticity, electrical conductivity, and single potential and rate of solution in various solvent liquids are changed. The absorption of a gas, too, may depend upon its condition; that is to say, the energy it possesses. For example, free hydrogen gas is very slightly absorbed by iron and some other metals, but hydrogen freshly liberated from combination either by electrolysis or by action of metal upon acid is very strongly absorbed by iron. Palladium, on the other hand, absorbs free hydrogen with great avidity.

SUMMARY.

In the absorption of water vapor by quartz flour, a soil separate, and typical soils, the rate of approach to equilibrium between soil and water vapor has been followed at various degrees of humidity, and these equilibrium points determined.

The amount of water absorbed increases with the humidity, but not in a simple mathematical relation.

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[a] Phil. Mag. (6), **5**, 521 (1903).

[b] Proc. Roy. Soc. London, **74**, 249 (1904–5).

[c] Loc. cit.

Toluene and other vapors were compared with water vapor, using the same soils, and show in general an absorption of the same order of magnitude.

The velocity of absorption decreases regularly as absorption proceeds, but it is not described by a simple logarithmic equation.

Relatively small decrease in vapor pressure produces a marked increase in the rate at which the soil dries out. At the moisture content known as "optimum" for plant growth, a rapid decrease in the rate of evaporation takes place, and at this particular moisture content there are likewise changes in other physical characteristics of the soil, such as specific volume, resistance to penetration, etc., which altogether point strongly to a purely physical reason for the existence of a narrow range of water content in a soil at which plants thrive best.[a]

The content of water in a soil at which plants begin to wilt is greater than the quantity of water the soil can take up from a saturated atmosphere. A heavy soil containing a high per cent of moisture may hold the water so absorbed that while the plant can get some water still it is by no means fully supplied.

The absorptive capacity of soil for water vapor is generally higher the finer the texture of the soil and the greater the content of humus. In general, productive soils have a very considerable capacity for water vapor.

Gases are absorbed to a different degree by each solid substance; the different soil components all possess a considerable absorption capacity, and mixtures of these constituents absorb gases additively; that is, each soil material exerts its absorptive effect independently of the rest of the soil about it. Soil constituents moistened with water absorb gases in greater quantity than would the same mass of water alone. Easily condensed gases are in general absorbed more easily.

Heat is evolved during the process of absorption, and this heat is greatly in excess of that given out by the condensation of the vapor to a liquid.

For equilibria between soils and atmosphere saturated with water vapor over a temperature range from 25° C. to 100° C., the amount of water absorbed decreases with increasing temperature. This confirms the results obtained by earlier investigators for the absorption of water vapor as well as for gases in general.

Absorbed gases are held with remarkable tenacity. Glass and minerals retain hygroscopic water up to 500° to 800° C.

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[a] See Cameron and Gallagher. Bul. 50, Bureau of Soils, U. S. Dept. of Agr., 1907.

Bodies which have been heated and then cooled in a vacuum show high absorptive power; consequently, absorption can not be looked upon solely as the solution of a gas in moisture films upon the grains of the solid.

In general, nitrogen is absorbed by soils in greater quantity than oxygen. This is especially interesting, since the absorption of oxygen and nitrogen from air by water gives a higher ratio of oxygen to nitrogen in the solution than the 1:4 relation which exists in air. The similar high absorptive power of aluminum hydroxide, ferric hydroxide, and magnesium carbonate for nitrogen indicates that this preference of soils for nitrogen is a real phenomenon, since these substances have no way of masking their true absorptive power for oxygen by converting it chemically to carbon dioxide, as a soil does, or to other oxides.

The absorption of carbon dioxide by soils is due in great measure to the presence of hydrated oxides, such as ferric oxide, and humus. Kaolin, calcium carbonate, and quartz also absorb carbon dioxide, but in comparatively small amounts.

Soils, whether acid or alkaline, dry or wet, absorb ammonia from the atmosphere in appreciable amount.

No one mathematical expression has been found to hold generally for the distribution of a gas between the vapor phase and absorbing solid. The specific attraction of solid and gas, the diffusion of gas into solid, the condensation of gas to liquids and consequent clogging of capillary channels where the forms and arrangement of these minute spaces enter to determine the vapor pressure of the liquid there enmeshed, all these factors complicate the observed relation of mass of gas adsorbed to mass of gas left in the vapor phase.

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Issued August 8, 1908.

U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF SOILS—BULLETIN No. 52.

MILTON WHITNEY, Chief.

ABSORPTION BY SOILS.

BY

HARRISON E. PATTEN AND WILLIAM H. WAGGAMAN.

WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1908.

BUREAU OF SOILS.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., February 13, 1908.

Sir: I have the honor to transmit herewith the manuscript of a technical paper entitled Absorption by Soils, by Messrs. Harrison E. Patten and William H. Waggaman of this Bureau.

In accordance with your suggestion, the manuscript has been submitted to Assistant Secretary Hays, who concurs with me in recommending it for publication as Bulletin 52 of the Bureau of Soils.

Respectfully,

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

PREFACE.

In the present bulletin Messrs. Patten and Waggaman have brought together the literature covering absorption of dissolved solids from liquid solutions, together with results of some important experimental investigations which have been carried on in this laboratory in continuance of the general work on soil absorption which has been under way for several years. The importance of this subject for practical soil work, for fertilizer manufacture, and for various technical processes has long been known, but it is only within the past few years that its importance has become generally recognized.

The principal object of this work has been to determine how absorption controls the concentration of the soil solution, which is the great nutrient medium upon which plants feed, and, further, to determine the effect of absorption upon the structure of the solid portion of the soil in modifying its power to hold and maintain the soil solution for the continued use of the plant. As a result of this work it has been shown that a number of modifying factors enter into each particular case, which makes it impracticable to formulate a simple general law which will account quantitatively for the distribution of a dissolved substance between the liquid solution and the absorbing medium, although it is brought out very clearly that under the ideal conditions, where there is no change in the surface of the absorbing medium, a simple mathematical law can be predicated a priori, which law is approximately realized in practice in those cases where it is known that the least amount of change takes place in the absorbing surface. The nature of these modifying factors, and in a general way the extent to which they enter, with especial reference to soil components, has been the subject of careful investigation, the results of which are here recorded.

In general it may be said that our knowledge of the nature and character of absorption factors and their influence upon the concentration of soil solution, and upon the reactions which take place between soil components and artificially added constituents, has been materially advanced, and that the further investigation of this important line of soil studies will be more easily and more rapidly prosecuted on the basis of the work presented in this bulletin.

Frank K. Cameron.

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ABSORPTION BY SOILS.

INTRODUCTION.

From the standpoint of soil chemistry the absorption of material from air and from soil solution is of the first importance. The absorptive power of the soil enables it to retain the soluble salts necessary to plant life in spite of the leaching effect of rains, thus storing up soluble material from the weathering and dissolving soil grains for future needs of crops. Also it prevents the soil solution from becoming too concentrated.

Besides this holding back of nutrient soluble salts, the absorptive power of a soil has an important part in determining its physical condition. There is a relation between the quantity of soluble salts absorbed by the soil and the size and compactness of the soil-grain aggregates; and upon the size and arrangement of these soil aggregates, in turn, the optimum water content of the soil depends. The openness of a soil determines its ventilation, and thus likewise its opportunity for securing proper oxidation and for the forming of humus. The optimum water content[a] as determined by plant growth coincides in general with the percentage of moisture at which the soil has its maximum volume, and at this maximum the soil also shows its greatest openness or minimum resistance to root penetration. Thus a purely physicochemical reason is at hand for the existence of an optimum water content in soils, and we are now able to correlate several of the factors which determine the state of a soil known as "good physical condition." Likewise, through its absorptive power the soil removes from soil solution and soil atmosphere the waste products thrown off by growing roots,[b] which products are detrimental or inhibitory to continued growth.

Appreciation of these relations has come about gradually. Sand filters for purification of sea water and impure drinking water have been used at least since the time of Aristotle; the removal of salts from sea water by percolation through sand or earth filters was practiced in Bacon's day. Dr. Steven Hales announced to the Royal Society in 1739 that the first portion of sea water passed through stone cisterns was pure. Berzelius filtered salt solutions through sand and found that the salt content was more or less removed; and Matteucie determined the concentration of salt in the solution after it had passed through successive filters, and found the concentration to be successively smaller. The clarification of barnyard liquor and other colored waters by percolation through fresh clay or loam was mentioned by Sir Humphrey Davy in 1813, by Gazzeri in 1819, Lambuschini in 1830, Browner in 1836, Huxtable in 1848, Bernays in 1849, and by Thompson and Way[a] in 1850. It is especially interesting to note that as early as 1819 Gazzeri considered that loam and clay take up in their pores the soluble matters in solution and retain them to release them by degrees to the plants. In 1830 Lambuschini suggested the name *incorporation* for the fixation of dung liquor by the soil, and in 1836 Browner insisted that soils held back even the soluble salts in dung liquor.

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[a] Bul. No. 50, Bureau of Soils, U. S. Dept. of Agr., 1907.

[b] Bul. No. 28, Bureau of Soils, U. S. Dept. Agr., 1905; Farmers' Bul. No. 257, U. S. Dept. Agr., 1906; Bul. No. 40, Bureau of Soils, U. S. Dept. Agr., 1907.

Liebig found that aqueous ammonia passed through clay lost its odor, and Thompson and Huxtable verified the experiment. In 1850 Way showed that soil likewise absorbed potassium, sodium, calcium, and magnesium, not only from solutions of their hydrates, but of their salts, with both strong and weak acids, the acid remaining in solution unabsorbed and combined with other bases leached from the soil. Phosphoric acid, however, was itself absorbed. Way believed the absorption or replacement of the bases to be total, but Voelcker showed that weak solutions of ammonia could circulate in the soil and still retain some of their ammonia unabsorbed, and Peters[b] demonstrated that however weak the solution used, potassium was never completely absorbed. Frank[c] confirmed Peters's results, using the percolation method. Thus there was introduced the conception of *distribution*, the partition of a soluble substance between solid and liquid, so that no matter how small a quantity of substance be present there is a fraction of it left in solution. And the application of this principle has led to a much better understanding of the retention of soluble material by soils.

Before proceeding to a detailed consideration of the different phenomena of absorption a few precise definitions are in order. The term absorption is used in general to designate the process by which a solid or a liquid draws unto itself and retains within its structure or on its surface another solid, liquid, or gas.

The simplest case of absorption is that of mechanical absorption, or *imbibition*, such as water held by a sponge, by porous solids like brick or charcoal, by powders, including soils, and by bodies which draw liquid or vapor into their most intimate recesses and swell, as, for example, starch with water, or rubber with chloroform.

A second kind of absorption is where a solid retains another solid so that the two form a *homogeneous body* and the mixture is either a

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[a] Storer, Agriculture, 1897, I, pp. 201 and 316; also Jour. Roy. Agr. Soc., **11**, 313 and 366 (1850).

[b] Landw. Vers.-Stat., **2**, 129 (1860).

[c] Ibid., **8**, 45 (1866).

definite chemical compound or a *solid solution*. The criterion of a solid solution is that when present in equilibrium with a liquid solution containing the same components a variation in the percentage of these components in the liquid is accompanied by a corresponding change in the composition of the solid phase. Thus free phosphoric acid added to a soil containing ferric hydroxide is absorbed in such a way that the more P_2O_5 there is in solution the more P_2O_5 is found in the solid ferric hydroxide—that is, the P_2O_5 forms a solid solution with the ferric hydroxide, and its composition changes with that of the liquid solution above it.[a] An even more interesting case is that of the absorption of phosphoric acid by lime. Here the P_2O_5 forms a solid solution with the CaO, the percentage of P_2O_5 in the solid phase increasing with increase of P_2O_5 in the liquid phase until a certain concentration in the liquid is reached, and further increase of P_2O_5 in the liquid causes no increase of P_2O_5 in the solid—that is, a definite compound of CaO and P_2O_5 has been formed.

A special case of absorption has been termed *adsorption*, which may be defined as the existence of a difference in concentration or density of a film adjacent to a bounding solid and the concentration or density of the mass of the liquid or gas which bathes this solid.

Whether this adsorbed film is in a liquid, solid, or gaseous state, or even loosely combined with the solid bounding medium, is not easily determined and has been the subject of much discussion. The change of state from solid to liquid and from liquid to vapor is very gradual. All the recent physical researches, dealing even with hard, polished "solid" surfaces, indicate a mobility of parts, an openness of structure, and a high power of retaining foreign material. But the ability of one body to hold another upon its surface is dependent upon the material of which each consists. So we are accustomed to say that adsorption depends upon the chemical constitution of the solid as well as of the substance adsorbed. Another way of stating the same idea is to attribute adsorption to a specific attraction between solid and adsorbed material.

This preference of one material for another is well shown by the separation of substances in solution from each other by simply percolating the liquid through an absorbent body, which takes one substance from solution, while the other passes into the filtrate. This process has been called *selective absorption* and is of very wide occurrence, although its possibilities as an analytical and technical method of separation are only beginning to be appreciated.

Throughout this paper the terms "solvent," "solute," and "absorbent" are used with the following meanings:

Solvent: A pure liquid used to dissolve some solid, liquid, or gas.

Solute: The substance dissolved by the solvent.

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[a] See Bul. No. 41, Bureau of Soils, U. S. Dept. Agr. The Action of Water and Aqueous Solutions upon Soil Phosphates. Frank K. Cameron and James M. Bell.

Absorbent: The solid body which when placed in a solution abstracts part or all of the dissolved material from the solution.

Further, the terms "gel," "sol," and "colloid" are used with special meanings:

Gel: A number of substances, such as metallic oxides, are precipitated from solutions of their soluble salts as amorphous solids. These solids frequently contain so much of the solvent from which precipitation takes place that they have a jellylike consistency, and consequently the term "gel" has been applied to them. When these gels are formed in an aqueous solution and the liquid held in combination with them is water, they are termed "hydrogels."

Sol: By proper treatment it is possible to cause these gels to redistribute or suspend themselves throughout the liquid from which they were originally precipitated. Such a resuspension of the precipitate in many cases has been found to consist of minute particles of the gel. Where this is the case the opalescent liquid thus formed is termed a "sol." Where the solvent used is water, such a suspension is termed a *hydrosol.*

A *colloid* has been defined as a material which when dissolved will not pass through certain membranes, and has been considered to be of high molecular weight and consequent complexity; a crystalline substance, on the other hand, passes through these membranes. This distinction between colloid and crystalloid is not maintained so rigidly at present, for some crystalline materials show a very slow rate of diffusion through the membranes. At present colloidal solutions are considered to be made up of minute particles in suspension. Consequently, if the absorption of materials from solution by finely divided solids is studied and the relation between this absorption and the formation of these particles into larger aggregates and their consequent settling from suspension, it is found that the general phenomena there observed are parallel to those where the much finer particles of a colloidal solution or precipitated colloid are under consideration.

The referring of various actions otherwise not clear to the presence of "colloidal material" does not now afford that satisfaction which it gave before the intimate relation between colloidal solutions and suspensions of larger particles had been recognized.

In order to bring out clearly the general application of the phenomena of absorption and the general principles derived therefrom, a number of solvents, solutes, and absorbents, in addition to soils and constituents of the soil solution, have been studied. The establishment of these general phenomena in the case of pure substances where no life process enters strengthens very greatly our certainty in their validity when they are found to hold good for such very complex materials as exist in soils and soil solutions.

RÉSUMÉ OF EARLIER WORK.

Hoffman[a] in 1858, summing up the question of removal of nutrient salts from a soil by rains, says:

> It is very probable that each soil possesses a peculiar power of retaining certain nutrient material for plants. But this power appears to have a limit, and whatever material over and above this limit remains in solution, follows the movement of this solution. In this movement of water itself there appears to be a means—at least for certain soils and certain relative positions—of returning to the earth a part of the leached soluble salts. When the rains are not heavy the water in the soil does not penetrate very deeply, and during the evaporation consequent upon hot weather the water from below is again drawn up to the surface and its soluble salts are returned to the fine soil grains.

In 1866 Frank[b] investigated the absorption of potassium chloride by soil. He used cylinders 3 inches in diameter and 3 to 6 feet long. The soil was carefully removed from the field and placed in these cylinders, keeping the same relative position of the soil layers. Distilled water was passed till only a trace of chlorine came through, as shown by a slight turbidity when silver nitrate was added. Then he placed 4 liters of potassium chloride solution, 1 gram per liter (0.1 per cent), in a flask and inverted it above the soil, so that the liquid might percolate under atmospheric pressure alone as the soil took it up, as illustrated in figure 1. He found that the salt solution drove out the water which remained in the soil, no diffusing of one liquid into the other being noticed. After he had made sure that the soil contained only salt solution, by analyzing the liquid which drained from tap No. 2, 12 inches below the surface of the soil, and finding that the same per cent of chlorine was in this liquid as in the original solution, he analyzed another portion of this same percolate and found that it contained only 9 per cent of its original potassium, 91 per cent being retained by 12 inches of soil. A similar test of the percolate from tap 3, 18 inches below the surface, showed 4.5 per cent of potassium left and 95.5 per cent absorbed. The taps lower down (4, 5, 6, etc.,) showed little further decrease in the potassium in the percolates, and even after the solution had passed through 6 feet of soil it always retained 2 to 2.5 per cent of its original potassium. So there appears to be a certain dilution of the solution—in this case 1 part in 40,000 to 50,000 parts—at which water is more effective in holding the dissolved material than the absorbing power of the soil.

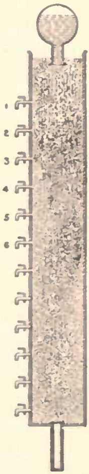

FIG. 1.—Percolation tube used by Frank in his studies on absorption.

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[a] Jahresb. Agr.-Chem., **1**, 16 (1858); see also Liebig, Ann. Chem. u. Pharm., **105**, 109 (1858); Grouven, Agron. Zeitung, 1858, p. 1; also Jahresb. Agr.-Chem., **1**, 14 (1858); Babos, Landw. Ber. v. B. (1858), p. 1.

Potassium is still more quickly absorbed from a solution of potassium sulphate, so that with a potassium sulphate solution it will not penetrate the soil so deeply as with a potassium chloride solution.

Frank found on using a solution of 1 gram pure potassium chloride and 1 gram sodium chloride to 100 parts of water that the potassium content of the percolate through 18 inches of soil still contained 18 per cent of its original potassium, as against 5 per cent (average) when no sodium chloride was present. Likewise, after passing through 4 feet of soil the percolate gave 5 per cent of the original potassium content, whereas with no sodium chloride in solution the potassium content was reduced to some 3 per cent of that in the solution added. Thus the presence of sodium chloride lowers the absorption of potassium and carries it deeper into the soil. In addition, a cylinder of earth which had been allowed to absorb potassium from a pure potassium chloride solution was percolated with distilled water till the runnings showed no potassium in solution. Then a solution of sodium chloride was passed through and potassium immediately appeared in the percolates. Frank was not at all sure that this points to a chemical substitution of potassium by sodium.

He found that the chlorine was absorbed from a sodium chloride solution percolated through earth and that most of the chlorine in the percolates was combined with sodium. It appeared to him, accordingly, that sodium chloride is not so easily decomposed by the earth as potassium chloride, and that a part of the sodium chloride is absorbed unchanged. Long-continued washing with pure water removed almost all the sodium chloride, while, as already stated, this can not be done in the case of potassium.

Next he tried the effect of sodium chloride upon the most insoluble phosphates in the soil. The upper 3 inches of soil in a cylinder filled with earth (as above described) was mixed with precipitated well-washed basic calcium phosphate and the cylinder percolated with distilled water. The filtration through these cylinders—4 to 6 feet long—took four weeks. At 12 inches below the surface only traces of phosphoric acid could be detected in the percolate; but, on the contrary, when sodium chloride solution (1 gram per liter) was passed through the soil phosphates were detected as far down in the cylinder as 4 feet and below.

Salomon[a] gives the absorption of calcium by various soils and soil constituents from several concentrations of calcium nitrate solution, to which was added sufficient ammonia to neutralize exactly the nitric acid of the calcium nitrate. The solution was placed with the soil in a flask, shaken, and allowed to stand forty-eight hours, filtered and analyzed and the absorbed calcium determined by difference. The results are given in Table I.

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[a] Landw. Vers.-Stat., **9**, 351 (1867).

TABLE I.—*Absorption of calcium from amoniacal calcium nitrate solution by soils, according to Salomon.*

		Used in experiment.		CaO in 200 c.c. solution added.	CaO remaining in 200 c.c. of solution.	CaO absorbed by 100 grams soil.
		Soil.	Solution.			
		Grams.	*C.c.*	*Grams.*	*Gram.*	*Gram.*
1	Soil from Möckern	100	200	0.1	0.0788	0.0212
2	do	100	200	.2	.1580	.0420
3	do	100	200	.4	.3096	.0904
4	do	50	100	1.0	.8120	.1880
5	Russian black earth	100	200	.1	.0848	.0152
6	do	100	200	.2	.1580	.0420
7	do	50	100	.4	.2344	.1656
8	do	50	100	1.0	.5960	.4040
9	White "Kujawischer"	50	100	.2	.1292	.0708
10	do	50	100	.4	.2701	.1299
11	do	50	100	1.0	.8586	.1414
12	Black "Kujawischer"	25	50	.2	.1071	.0929
13	do	25	50	.5	.2862	.2138
14	do	25	50	1.0	.6979	.3021
15	Kaolin from Salzmunde	50	100	.2	.1743	.0257
16	do	50	100	.5	.4306	.0694
17	do	50	100	1.0	.8619	.1381
18	Tile clay	50	100	.2	.1704	.0296
19	do	50	100	.5	.3500	.1500
20	do	50	100	1.0	.7326	.2674
21	Ferric hydroxide	25	50	.2	.0490	.1510
22	do	25	50	1.0	.0576	.9424
23	Aluminum hydroxide	50	100	.2	.0000	.2000
24	do	25	50	.5	.0226	.4774
25	do	25	50	1.0	.309	.9691
26	Silicic acid (hydrated)	50	100	.2	.0659	.1341
27	do	50	100	.5	.1664	.3335
28	do	50	100	1.0	.2388	.7612
29	Kaolin+aluminum hydroxide, equal parts	50	100	.4	.0106	.3894
30	100 grams kaolin+25 grams ferric hydroxide	125	200	1.0	.3480	.6520
31	50 grams kaolin+50 grams ferric hydroxide	100	200	1.0	.0435	.9565
32	Soil from Möckern	50	200	1.0	.8772	[a].1228
33	Russian black earth	50	200	.5	.2184	[a].2816

[a] Effect of mass of earth used.

The behavior of the Russian black earth, which contains 9 to 15 per cent of humus, compared with those soils poor in humus, shows that the humus in the Russian black earth must be already saturated with bases. Salomon's predecessor, Pochwistneff, had already found by direct investigation that this is the case and that the black earth contains calcium humate. The soil from Möckern shows a lower absorption than the black earth for a solution containing 0.5 gram calcium oxide per liter, and both soils show the same degree of absorption for a 1-gram calcium oxide per liter solution. The other soils, as, for example, the white "Kujawischer" soil, which contains hardly a trace of humus, nevertheless show an absorption for calcium nearly equal to that of humus-rich soils, such as the black "Kujawischer" and the Russian black earth.

The similarity between the Russian black earth and the tile clay—in that both show a change in absorption with increasing concentration—suggests that the cause can not be in the humus content of the black earth. Salomon considers that such a calcium solution as was used would probably not act upon humic acid which had been already saturated with bases and would probably be changed only where free humic acid, or humic acid dissolved in carbon dioxide and alkalies, is present.

It is evident that all the solute is not withdrawn from the solutions even at low concentrations; apparently the aluminum hydroxide absorbs all the calcium from a 0.1 per cent solution, but this exception to the general rule was doubtless due to the presence of ammonium carbonate in the alumina, which precipitated the calcium as carbonate. The aluminum hydroxide was prepared from aluminum sulphate by ammonia and washed with ammonium chloride.

The white "Kujawischer" soil (entirely free from calcium) absorbed almost the same mass of calcium from a 0.2 per cent solution as from a 0.5 per cent solution. This means that the absorption capacity is limited. The black "Kujawischer" soil shows a similar tendency toward an absorption limit.

Biedermann [a] prefaces a research on absorption as follows:

> Since it has been made clear that of itself the chemical analysis of a soil can give no indication as to its value in respect to cultivation and crop yield, one is forced to study the properties of the soil in other ways, and thus it is soon discovered that the absorptive power of the soil for soluble fertilizers—the ability to fix the same and then to give them up to the plants—is of great significance for practical agriculture as well as for the interesting philosophical question, In what form do the plants obtain their nourishment from the soil?

Biedermann studied the absorption of potassium and of phosphates by soils, and he showed the magnitude of the absorption effect for a number of soils. He concludes that chalk, magnesia, and sulphuric acid do not affect absorption by the soil, and suggests that by use of a suitable solute the absorptive power of a soil may be determined—possibly by potassium phosphate. He tried potassium carbonate solution, percolating it through different soils and titrating the liquid passed through with sulphuric acid, but the results were unsatisfactory.

The quantities of potassium absorbed by different soils vary considerably, and it is certain that the magnitude of absorption is in accord with the value of a soil, although neither the quantity of bases extracted from the soil by means of ammonium tartrate-oxalate solution, nor the ferric hydroxide or aluminum hydroxide content of the soil, nor the quantity of humus in the soil—as shown by weight loss on ignition—give a certain indication of the soil's productive power.

Treutler [b] in a series of researches has studied the absorption and resolution of potassium by soils as affected by other fertilizer agencies. In all his work he used cylinders 9.7 cm. wide and 90 cm. long. Into each cylinder was shaken 4 pounds of earth (containing 85.5 per cent of fine earth), and then 0.5 pound of earth was rubbed up with the potassium salt and with the fertilizer, whose effect upon the absorption of potassium it was desired to study. The 4.5 pounds of earth had a depth of 29 cm. in the cylinder. In each experiment the earth was weighed air dry. The quantity of potassium salt was so chosen that exactly 1 gram of potassium oxide was added to the 4.5 pounds of earth. For comparison blank experiments were made, using each potassium salt alone and the cylinder then percolated with distilled water to ascertain the per cent of potassium the earth would absorb. The 4.5-pound portion of soil required 672 cm. of water to saturate it, so that in each experiment 1,672 c. c. of water were passed through the soil in order to obtain a liter of percolate. This same percolate was repassed through the soil 12 times in order to obtain the equilibrium conditions. Table II is compiled from Treutler's results:

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[a] Landw. Vers.-Stat., **11**, 1, (1869).

[b] Landw. Vers.-Stat., **12**, 184 (1869); **15**, 371 (1872).

TABLE II.—*Effect of various fertilizers upon the absorption of potassium by a soil, compiled from the results of Treutler.*

[Four and one-half pounds of earth 29 centimeters deep, percolated 12 times with the same percolate, 1,672 cubic centimeters in volume, to insure equilibrium.]

Fertilizer added in top 0.5 pound of soil.	Potassium absorbed.			
	1.849 grams K_2SO_4 added.	2.146 grams KNO_3 added.	1.583 grams KCl added.	1.467 grams K_2CO_3 added.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Bone dust, 500 grams	45.3	54.43	58.0	51,52
Bone dust, 50 grams	81.6	95.09	79.8	98.00
Humus soil, 250 grams	83.4	95.12	80.7	98.13
Cow manure, 80 grams	89.7	92.21	82.2	97.00
Sheep manure, 80 grams	93.2	89.74	90.5	90.31
Horse manure, 80 grams	93.0	93.62	91.3	85.63
Cow urine, 125 grams	96.3	90.68	91.5	94.99
Chili saltpeter, 20 grams	86.3	86.83	....	83.75
Ammonium carbonate, 20 grams	88.7	89.61	85.0	88.37
Superphosphate, 20 grams	89.6	87.90	86.1.	91.98
Magnesium sulphate, 5 grams	90.2	83.52	....	96.76
Gypsum, 20 grams	90.4	90.01	88.6	93.05
Humus soil, 250 grams + $(NH_4)x(CO_3)y$, 20 grams	91.8	82.25	88.7	94.65
Water containing carbon dioxide, 1 liter	93.7	94.96	92.9	95.62
Potassium magnesium sulphate, 3.698 grams	93.9	84.29	....	89.07
Sodium chloride, 10 grams	96.4	90.90	95.4	[a] 100.00
Distilled water alone passed through soil	[b] 97.9	[a] 91.75	[b] 94.7	[a] 97.60

[a] Landw. Vers.-Stat., **15**, 372 (1872).

[b] Landw. Vers.-Stat., **12**, 191 (1869).

Treutler found that the greatest quantity of potassium was absorbed from the sulphate, the carbonate, chloride, and nitrate following in the order named, and he concluded, therefore, that a deeper penetration of potassium into the soil was secured by the use of potassium chloride than by the use of potassium sulphate as a fertilizer. He found, further, that the relative absorption from these two salts was not materially affected by the addition of other salts and of the common fertilizers. The absorption of the potassium from the carbonate and nitrate is more affected by other agencies than is the absorption from the sulphate or from the chloride, the absorption from the carbonate being affected to the greatest extent.

In general, the addition of other mineral salts depressed the absorption of potassium, a marked influence being noticed in the case of sodium chloride, which further brought into solution in the soil percolate noticeable quantities of magnesium salt; and for this reason Treutler concludes that sodium chloride is harmful rather than beneficial as a fertilizer.

Bone dust and superphosphate depress the absorption of potassium; and Treutler considers them especially useful on this account, as they tend to increase the concentration of potassium salts as well as of phosphoric acid and ammonia in the soil solutions. Gypsum and magnesium sulphate were found to increase the concentration of potassium in the percolate. Humus, and especially humus mixed with ammonium carbonate, appeared to decrease the absorption, which effect is attributed to the formation of large quantities of carbon dioxide from the humus.

Knop[a] includes under absorption the process of conversion of a solid first to soluble form and then the spreading of the substance upon the soil grains in such a way as to withdraw it from solution, regardless of whether chemical affinity or surface attraction is the cause of this retention or whether the substance absorbed is decomposed chemically or absorbed unchanged. He used a solution of 1 gram ammonium chloride in 208 c. c. of water to determine the absorptive power of a soil. One hundred grams of earth were taken for analysis. The nitrogen corresponding to the ammonia still left in solution was determined and the number of cubic centimeters of nitrogen absorbed by the soil taken as the measure of the absorptive power of the soil. Using this method, he found the absorption of ammonia by 38 soils which had been analyzed chemically.

In a few cases he compared the absorption of potassium with that of ammonia. For this purpose he employed an analytical procedure which has since been followed by a number of investigators. These two analytical methods for ammonia and for potassium are given in detail here, since a number of investigators have used them to express their data on the absorption by soils in terms of Knop's absorption figure, i. e., the cubic centimeters of nitrogen (as ammonia) absorbed by 100 grams of soil, from 200 c. c. of the ammonium chloride solution described above. A potassium carbonate solution was taken of such concentration that 100 c. c. contained exactly the weight of potassium equivalent to 100 c. c. of nitrogen gas. Fifty cubic centimeters of this solution plus 50 c. c. of the above ammonium chloride solution when evaporated to dryness gave all the potassium as chloride, the ammonia and carbon dioxide going off upon ignition. But when one adds 100 c. c. of the ammonium chloride solution to 50 c. c. of this potassium carbonate solution and evaporates to dryness there remains sufficient ammonium chloride to give by the nitrometer method 50 c. c. of nitrogen. This fact was made the basis for a quantitative estimation of the potassium by adding ammonium chloride to the potassium carbonate solution, evaporating, and then determining the nitrogen in the residue.

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[a] Knop's book, Die Bonitirung der Ackererde, published by H. Haessel, Leipzig, 1872, 2d edition, is not generally available. We are indebted to the Massachusetts State Experiment Station, Amherst, for the use of their copy.

Knop believed that the absorptive power of a soil was proportional to the "Aufgeschlossene Silicatbasen," i. e., such substances as ferric oxide, alumina, etc. His data, on the whole, seems to bear out this conclusion. But later investigators[a] have shown that this is by no means the sole factor to be considered; and, indeed, Knop himself admitted this. He found the absorption for one and the same soil a constant, but seems to have no clear idea of the effect of end concentration of solution upon the quantity of solute absorbed. While he recognizes that substances in a soil capable of forming well-defined chemical compounds will of course absorb from a solution the material with which they can combine, he still observes phenomena in the absorption of potassium and of ammonia which he can not explain in the ordinary chemical way. He thinks the absorption of phosphoric acid may be explained as due to chemical combination, and if it were merely a question of the absorption of caustic potash or of ammonium hydroxide he would class these also as reacting chemically with the soil. But he finds that the selective absorption—the separation of these bases from the strongest acids by soil—and the effects upon absorption produced by varying quantities of soil, of solvent, and of solute all complicate the problem so much that he can not give a simple chemical explanation of it. He shows, too, that the power of a soil to absorb moisture from the air parallels in general its absorption of ammonia from ammonium chloride solution.

Frey[b] continued the work of Knop and confirmed his results.

Pillitz[c] showed that soils possess a saturation point for ammonia absorbed from ammonium chloride solution, and Fesca[d] recognized the influence of extent of soil grain surface in determining the absorption capacity. In 1887 Kellner[e] confirmed Pillitz's experiments and from new work concludes that ammonia and potassium are absorbed in chemically equivalent quantities by soils. Kellner extracts absorbed potassium from a soil thus: The soil (20 grams) is heated with 50 c. c. saturated ammonium chloride solution for a half hour, the solution poured off, the soil washed with hot distilled water, and fresh ammonium chloride solution added to the soil. This extraction is repeated (fifteen to twenty times) until the filtered solution leaves no solid residue upon evaporation and ignition. In this manner he recovers slightly more potassium than the soil had taken up from a known potassium chloride solution. This recovery is especially interesting since Way[a] and Eichorn, Dietrich,[b] Peters,[c] and Schuhmacher[d] were all unable to substitute completely one absorbed base by another. This method of substitution used by Kellner is essentially a percolation, and recognizes in a practical way the distribution of potassium between soil and solution. He also suggests that absorbed potassium may be more firmly fixed in an insoluble form, as, for instance, by internal arrangement of the double silicates containing water.[e] He further concludes that for potassium and calcium it may be considered as settled that these elements can afford nourishment to plants only when in dissolved or in absorbed condition.

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[a] See Sachsse, Lehrbuch der Agrikulturchemie, p. 169. "Mehr als eine gans grobe Annäherung an ein Verhältniss zwischen aufgeschlossenen Silikatbasen und Absorption lässt sich nicht erwarten."

[b] Landw. Vers.-Stat., **18**, 3 (1875).

[c] Zeit. anal. Chem., **14**, 55, 285 (1875).

[d] Die agronomische Bodenuntersuchung und Kartirung, 1879, p. 28.

[e] Landw. Vers.-Stat., **33**, 359 (1887).

Fiedler[f] has investigated the effect of sodium nitrate upon the absorption of phosphoric acid and potassium by soils. He concludes that the sodium nitrate prevents the percolating soil moisture from carrying phosphoric acid down with it to lower levels. On the other hand, potassium is less absorbed in the presence of the sodium nitrate and is carried deeper into the earth. When calcium is present in the soil in goodly quantity, this effect of sodium nitrate upon the potassium is not observed, while the sodium nitrate still is able to act upon the phosphate to prevent its removal by leaching. Fiedler suggests that as the quantity of sodium nitrate is increased more calcium nitrate is formed, and that this precipitates the phosphoric acid of the soluble phosphates as insoluble calcium phosphate.

Van Bemmelen,[g] in 1888, sums up the results of an extended research upon the absorption of soluble material from solution by soils and soil constituents as follows:

> Absorption compounds are formed from their components according to inconstant molecular ratios. They must be distinguished from chemical compounds, although they may often be rearranged into definite chemical individuals. Colloidal substances form such absorption compounds with water or other liquids, and with bases, acids, and salts when in contact with their solutions. The absorptive power of a colloid depends upon its molecular state of aggregation, and is also different for the different

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[a] Jour. Roy. Agr. Soc., **11**, 313 (1850).

[b] Jahresb. Agr. Chem., **1**, 29 (1858); **5**, 12 (1862).

[c] Ibid., **3**, 11 (1860).

[d] Ibid., **10**, 21 (1867).

[e] Landw. Vers.-Stat., **33**, 364 (1887).

[f] Landw. Vers.-Stat., **26**, 135 (1881).

[g] Landw. Vers.-Stat., **35**, 136 (1888).

substances which it absorbs. The power of absorption decreases as the colloid holds absorbed more and more of the substance. The relation between the concentration in the colloid and the concentration in the solution at equilibrium is a complex function (still unknown) of these concentrations and of the temperature. The absorbed substances may be substituted by other substances absorbed from solution by the colloid; bases may in this manner be substituted for the bases of a salt solution. Colloids may often produce chemical decomposition of salts by their power of absorption. The soil contains colloids, colloidal silicates, iron oxide, silicic acid, and humus substances, all of which may bring about these actions.

Van Bemmelen thinks that the absorptive power of a soil is mainly to be ascribed to the colloidal oxides and silicates present in it.

Humus substances are decomposition and degradation products of carbohydrates, albuminoids, etc. Humus will absorb ammonia and organic materials to a greater or less degree. Natural humus contains nitrogen, of which a part may be driven off as ammonia by dilute potassium hydroxide; on treating further with strong potash solution ammonia is unmistakably given off anew. He states that when peat is analyzed it shows the presence of alkali bases, which for the most part must be absorbed, since the peat is lacking in mineral acids sufficient to neutralize them.

Consideration of the solubility of the humus substances shows that some exist which are of themselves soluble in water. Some, indeed, according to Van Bemmelen, may go through colloidal membranes on dialyzing, but for the most part their solubility is a colloidal solubility. They form generally opalescent liquids when they are dissolved. Frequently the solubility depends upon small masses of alkali or of ammonia. Often the humus constituents may be separated by the influence of a small mass of acid or salt or by drying, as well as in other ways changed into an insoluble modification—as is true for colloidal substances in general.

Many dissolved humus substances show the properties of a hydrogel. The substance when dissolved by an alkali and coagulated by an acid after washing out partly dissolves again, and this solution is of a colloidal nature. These humus substances form absorption complexes with acids and salts, but most easily with bases. The dissolved humus substances form with alkalies soluble complexes which may be separated by alcohol.

Heiden[a] found that peat and various preparations of the supposed humic acids when brought into solutions of chloride of potassium and chloride of ammonium remove a portion of these salts from the liquid, leaving the solutions perceptibly weaker. The removed salts were for the most part readily recovered by a small quantity of water. Schumacher[b] observed that humus artificially prepared by the action of oil of vitriol on sugar when placed in 10 times its quantity of solutions of various salts containing about 0.5 per cent of solid matter absorbed of sulphates of soda and ammonium and of chlorides of calcium and ammonium about 2 per cent, of sulphate of potash 4 per cent, and of phosphate of soda 10 per cent. Schumacher also noticed that sulphate of potash is able to expel sulphate of ammonium from so-called humic acid which has been saturated with the latter salt, but that the latter can not displace the former. In Schumacher's experiments pure water freely dissolved the salts absorbed by the supposed humic acid.[a]

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[a] Hoffmann's Jahresb., 1866, p. 29.

[b] Hoffmann's Jahresb., 1867, p. 18.

A neat experimental demonstration of the absorption of soluble material from solution was given in 1867. Humus and a weak solution of oxalic acid were placed in a beaker.[b] The humus absorbed the oxalic acid from solution, and after the humus had settled and the supernatant solution had become clear a little sack made of collodion, attached to a glass tube and filled with water and calcium carbonate, was suspended in the solution, not touching the layer of settled-out humus. The oxalic acid of the solution diffused into the collodion sack and reacted with the calcium carbonate to form insoluble calcium oxalate. Thus the concentration of the solution in oxalic acid is lowered and the absorbed oxalic acid from the humus comes again into solution, and finally the absorbed oxalic acid is practically all removed from the humus. This was shown by removing the humus and extracting with hot water. The filtrate showed no trace of oxalic acid. The humus was free from bases, so that a chemical combination could not have been formed. If the humus had been in contact with a nutrient solution, and had absorbed plant food from it, a plant whose roots were in the solution would have behaved in a similar manner, absorbing the soluble matter from solution just as did the collodion sack containing calcium carbonate.

From calcium phosphate, humus suspended in water can absorb calcium and considerable free phosphoric acid.

That plant substances and animal tissues may absorb inorganic chemical compounds accompanied even by chemical decomposition of inorganic solute is known. Consequently one may expect of the humus constituents that they are in condition to absorb whole salts and acids in small amounts. If these humus constituents are coagulated from aqueous solution by a small mass of acid or salt, they are very difficult to free of acids or salts by washing. This fact van Bemmelen considers as showing that the acid or the salt is absorbed by a colloid.[c]

According to van Bemmelen, compounds of the so-called humic acid soluble in water are obtained when the aqueous or alkaline solution of a humus substance is treated with a solution of the hydrates of the alkaline earths or salts of the alkaline earths and metallic oxides—for instance, calcium, lead, and iron, etc. These compounds are also of colloidal nature and of changing composition. The humus substance in aqueous solution is coagulated and precipitated by a small mass of salt, and may fix a certain mass of base by absorption. Even an undissolved base in a hydrogel condition may precipitate humic acid, as, for instance, the hydrogel of alumina.

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[a] Hoffmann's Jahresb., 1867, p. 18. See also Johnson, How Crops Feed, p. 172.

[b] Quoted by Schumacher, Physik der Pflanze, p. 304, Berlin, 1867.

[c] Van Bemmelen, Landw. Vers.-Stat., **35**, 69 (1888).

The humus substances hold the potassium more strongly combined than the calcium, but the calcium compound is less soluble. If, therefore, humus is treated with a solution of a potassium salt, a certain mass of potassium is fixed, along with an interchange with calcium and magnesium; and if the soluble compound of humus is treated with an alkali or calcium solution, then it will form an insoluble calcium humus compound. The action of humus substances upon alkali carbonates, alkali phosphates, and, in general, salts of weak acids, is such that certain masses of alkali are absorbed with exchange for calcium and magnesium. In addition, alkali is absorbed by the insoluble humus substances, humus substance is brought into solution by the alkali thus set free, and the above mineral acids are precipitated by alkaline earths. Since, in general, the absorption of base is greater than of acid, the remaining solution has an acid reaction, although the salt was one of a strong base with a weak acid.

The decolorizing action of wood charcoal was discovered in 1791 by Lowitz,[a] and later Figuier showed the greater absorbing power of animal charcoal. Payen[b] found that charcoal could absorb lime from solution as well as coloring matter. Graham[c] ascribed this decolorization to the concentration of coloring matter upon the surface of the carbon—that is, to adsorption—a purely mechanical explanation. He found that charcoal also acts chemically upon solutions, extracting the metal from solutions. Weppen[d] found that one salt affects the absorption of another by charcoal. Birnbaum and Bombasch[e] found that boneblack absorbs a small amount of ammonia from ammonium salts and that in other cases the acid and basic radicals are absorbed, but not in equivalent proportions. Qualitative experiments by Liebermann[f] have shown that the acidity or basicity of a solution treated with charcoal changes as well as the concentration. Similar results have been obtained by Moride,[g]

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[a] See Ostwald, Stoechiometrie, 1891, p. 1093.

[b] Ann. Chim. Phys., **21**, 215 (1822).

[c] Quarterly Jour. Sci. (new series), **7**, 120 (1830); also Pogg. Ann., **19**, 139 (1830).

[d] Ann. Phys. Chem., **55**, 241 (1845); **59**, 354 (1846).

[e] Dingl. Poly. Jour., **218**, 148 (1876).

[f] Wien. Akad. Ber., **74**, 331 (1877).

[g] Compt. rend., **41**, 605 (1855).

Esprit,[a] and Heintz,[b] and Kelberin[c] has studied the absorption of hydrochloric acid by charcoal. Kroeker[d] and Lagergren[e] have used charcoal in studying the distribution of the solute between the solvent and absorbent, and the latter investigator used charcoal in studying the rate of absorption. Oechsner de Coninck[f] has shown that heavy metals are removed from solution of their salts by charcoal.

Rosenthaler and Türk[g] have studied the absorption of various pharmaceutical substances from their solutions when treated under standard conditions with different kinds of charcoal. These charcoals may be divided, according to their absorbent powers, into strongly absorbent—bone, flesh, and "vegetable blood" charcoals, in the order named—and weakly absorbent or nonabsorbent—blood, lime-wood, and spongy charcoals. For the same kind of charcoal the absorption of any substance varies with the solvent which is employed. The absorption is by far the strongest in aqueous solutions; it is less with ethyl alcohol, methyl alcohol, ethyl acetate, acetone, and least of all with chloroform solutions. The speed of absorption depends on the same factors as influence the amount of absorption, being greatest in the case of bone charcoal and aqueous solutions. The quantity of substance absorbed by a given quantity of charcoal is relatively less for concentrated solutions than for dilute solutions. All the circumstances which favor absorption act in a similar degree in resisting the reextraction of the absorbed substance. The decolorizing power of the charcoal is dependent on its absorbing power. As regards the use of charcoal for decolorizing purposes, the authors state that the charcoal must be carefully purified before use, either by repeated extraction with the solvent which is to be used or by igniting gently and washing with acid. The quantity of charcoal employed should be as small as possible. It is not necessary to heat the liquid with the charcoal; several hours' contact at the ordinary temperature will suffice. The decolorization should not, for preference, be effected in an aqueous solution, because the loss of substance by absorption is at a maximum with that solvent; the solution should be as concentrated as possible. Easily oxidizable substances should not be decolorized by animal charcoal, because this charcoal has a powerful oxidizing action; the oxidation of alkaloids is retarded by treating them in the form of salts. Blood charcoal has the strongest oxidizing action, lime-wood charcoal has hardly any. Bone and flesh charcoals can be employed in the determination of caffeine without loss of alkaloid, but in the determination of sugars, etc., in wine and other liquids charcoal should not be used unless it has been proved that no loss by absorption takes place under the conditions of the experiment. The close interdependence of the decolorizing and absorbent properties of charcoals suggests that the decolorization is due to absorption of the coloring matters. The fact that successful results can be obtained in practice depends, first, on the circumstance that the amount of coloring matter is generally only a fraction of the total substance in solution, and, second, on a selective absorption, according to which the quantity absorbed is generally proportional to the molecular weight, most coloring matters being substances of high molecular weight.

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[a] Jour. pharm., **16**, 192 (1849).

[b] Lieb. Ann., **187**, 223 (1877).

[c] See Ostwald, Lehrbuch der Allgemeine Chemie (1891) p. 1096.

[d] Uber die Adsorption gelöster Körper durch Kohle, Diss. Berlin, 1892.

[e] Bihang till K. Sv. Vet. Akad. Handl., **24**, Afd. II, No. 4 (1898).

[f] Compt. rend., **130**, 1627 (1900).

[g] Arch. Pharm., **244**, 517 (1906).

The experiments of Kellner[a] show that platinum black absorbs minute quantities of acids and alkalies, but gives them up to water on standing.

Many rock powders possess the power of absorbing the coloring matter from solutions in which the powders are suspended. The alkalinity of water in which rock powders have been in suspension has been shown in a large number of cases by Clarke.[b] Some powders, such as very finely powdered orthoclase, have been found to show no red color with phenolphthalein. This is due to the absorption of the color by the powder. A suspension of orthoclase in water which showed no color on the addition of phenolphthalein was allowed to settle, and the supernatant solution after being poured off showed a distinct red color with a further addition of phenolphthalein. When a little of the suspended material was added to the solution again the red color disappeared from the solutions, but was seen on the surface of the solid particles. The test of alkalinity of a solution by phenolphthalein can not properly be made if there are present in suspension finely divided particles which have the power of absorbing the indicator. Another substance which absorbs the phenolphthalein is magnesium ammonium phosphate.

Hulett and Duschak[c] have investigated the nature of barium sulphate precipitates, which are nearly always found to weigh too much, and attribute the results observed by them to the formation of a compound $BaCl.HSO_4$. On long standing or heating of the precipitate hydrochloric acid was given off—which is in harmony with the assumption that hydrochloric acid was absorbed on the surface of the precipitate and escaped when the area of surface was reduced. Barium sulphate precipitates have been found to absorb many compounds from solution. Vanino and Hartl[a] observed that this precipitate absorbs colloidal metals from solution, and Patten[b] observed that salts of nickel, cobalt, chromium, iron, and manganese in solution are absorbed by barium sulphate precipitates. Korte[c] has found that not only does barium sulphate absorb salts from solution, but also calcium oxalate precipitates absorb magnesium oxalate, even in the presence of ammonium chloride, and ferric hydroxide absorbs manganese hydroxide and nickel hydroxide. Ostwald[d] has called attention to similar cases.

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[a] Ann. Phys. Chem., **57**, 79 (1895).

[b] Bul. No. 167, U. S. Geol. Survey, p. 156 (1900).

[c] Zeit. anorg. Chem., **40**, 196 (1904). See also Trans. Am. Electro-Chem. Soc., **12**, 257 (1908).

Suida[e] has shown that the fixation of dyes by animal textiles (wool or silk) is due in part to the amphoteric character of the amino acids which enter into the composition of these albuminoid bodies. He has separated bodies from these complex albuminoid fibers which, like the original substance, fix acid or basic dyes, since these simpler decomposition products are themselves amino acids, $R(NH_2)(COOH)$.

Colloidal substances have the power of absorption to a very marked degree. In numerous papers[f] van Bemmelen has shown that all colloids absorb organic and inorganic compounds. They have the power of absorbing one of the constituents of an inorganic salt, leaving the solution acid or alkaline, as the case may be. The distribution of the absorbed material between water and the colloid is not constant, but depends upon the concentration of the solution.

The use of clays as absorbents has been specially valuable in technical processes, and more especially in the clarification and separation of oils. The technical literature on this subject is now enormous, but, while of the highest importance for certain commercial processes, the work which has been done adds comparatively little to our theoretical knowledge of the subject, and hence is not given in detail.

SELECTIVE ABSORPTION.

It has been found by numerous investigators that when an absorbent is brought into contact with a solution containing two or more solutes these solutes may be absorbed in very different degrees, and thus more or less complete separation of the solutes may be effected. A particularly interesting case of selective absorption is where a substance like a salt is separated into its constituent parts and either the acid or the base from which the salt is derived is absorbed to a greater extent, leaving the solution more concentrated with respect to the least-absorbed constituent. Thus, for instance, a solution of potassium chloride agitated in contact with a soil, or cotton, or carbon black, or similar materials which do not themselves react with either the base or the acid, nevertheless leaves a solution which is markedly acid. This phenomenon is particularly marked in the case of such salts as are greatly hydrolyzed when brought into contact with water.

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[a] Ber., **37**, 3620 (1904).

[b] Jour. Am. Chem. Soc., **25**, 186 (1903).

[c] Jour. Chem. Soc., **87**, 1503 (1905).

[d] Foundations of Analytical Chemistry, Trans. by McGowan, 1895, p. 26.

[e] Monatsh. Chem., **25**, 1107 (1904); **26**, 413, 855 (1905); **27**, 225 (1906); Hoppe-Seyler's Zeit. physiol. Chem., **5**, 174 (1906); C. f. the literature on dyes and amino acids given there.

[f] Landw. Vers.-Stat., **35**, 72 (1888); Jour. prakt. Chem., **23**, 324 (1881); Zeit. phys. Chem., **18**, 331 (1895); Zeit. anorg. Chem., **13**, 233 (1896); **18**, 14, 98 (1898); **23**, 111, 321 (1900); **30**, 265 (1902); **35**, 23, 338 (1904); Arch. Néer. (2), **6**, 607 (1903).

A third type of selective absorption has been observed in a few cases and designated as negative absorption—that is, there is an increase in the concentration of the solute after contact with the absorbent. This is obviously due to the fact that the solvent is taken up or absorbed to a relatively greater extent than the solute. This perhaps theoretically should not be considered as a special case, since we are yet without criteria to distinguish between solvent and solute, and it is rather a matter of convenience to consider the material in excess as the solvent.

CARBON.

SEPARATION OF SILVER FROM SILVER NITRATE.

Graham[a] studied a number of interesting cases of selective absorption. He found, for instance, that when a solution of silver nitrate was passed through powdered charcoal a separation of the salt was effected, and a subsequent examination of the charcoal disclosed the presence of metallic silver in small spangles.

EXTRACTION OF METALS FROM NEUTRAL SALT SOLUTIONS.

Esprit,[b] Moride,[c] and Heintz[d] obtained similar selective absorptions with carbon, the metal being extracted from its neutral salt solution and the resulting solution having in consequence an acid reaction.

Oechsner de Coninck[e] effected separations of the heavy metals from their solutions by percolating through charcoal. In this way iron could be quantitatively separated from solutions of its chloride.

LIBERATION OF ACID FROM NEUTRAL SALT SOLUTIONS.

Liebermann[f] found that the following salt solutions passed through animal charcoal yielded acid solutions, some of which on distillation gave the free acid: The barium salt of the acid formed by oxidizing glycerin with chromic acid, barium formate, sodium acetate, lead acetate, calcium glycollate, zinc lactate, ammonium oxalate, sodium-potassium tartrate, sodium borate (previously alkaline), trisodium phosphate (previously very alkaline), disodium phosphate, ferrous sulphate, copper sulphate, silver nitrate, and potassium acetate. The following aqueous salt solutions, however, showed no change of alkalinity or acidity, but the concentrations were less after passing through carbon: Sodium chloride, nitrate, and sulphate; potassium chloride, iodide, bromide, cyanide, sulphocyanate, and sulphate; calcium chloride, and barium chloride and nitrate. In the case of morphine acetate and caffein citrate, the first percolates contained none of the solute, but after a time the free acids came through.

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[a] Pogg. Ann., **19**, 139 (1830).

[b] Jour. Pharm., **16**, 192 (1849).

[c] Compt. rend., **41**, 605 (1855).

[d] Lieb. Ann., **187**, 227 (1877).

[e] Compt. rend., **130**, 1627 (1900).

[f] Wien. Akad. Ber., **74**, 331 (1877).

SEPARATION OF ORGANIC DYES INTO ACID AND BASIC CONSTITUENTS.

Freundlich and Losev [a] have found that basic dyes in aqueous solution are split by charcoal, the base being absorbed and the acid remaining as such in solution. The absorbents silk, wool, and cotton act similarly. The color base of crystal violet present in adsorbed condition upon the surface of the charcoal is a glittering brown-violet color; it is insoluble in water, but dissolves in acids, alcohols, pyridine, etc., with a blue-violet color. The color-base of "Neufuchsin" appears green on the surface of the charcoal and dissolves in acids, alcohols, pyridine, etc., with a red color. The body, described by Baeyer, obtained when fuchsine is treated with cold aqueous sodium hydroxide, and which is regarded as a polymeric imine base, resembles in many respects the material adsorbed on the charcoal. From crystal violet, also, there was obtained, by adding cold sodium hydroxide solution, a brown-violet amorphous powder difficultly soluble in water, but readily soluble in alcohols and pyridine with a blue-violet color. On these experimental grounds Freundlich and Losev suggest that amorphous polymerization products of the color base are adsorbed and form with carbon or other adsorbent, colloid complexes. In the case of the dyes patent-blue and orange IV, there is no splitting of the dye salt by charcoal on adsorption.

GELATINE.

SEPARATION OF ALUMINA FROM ITS SALTS.

Lummiere and Seyewetz [b] found that the separation of alumina from its salts could be effected by using gelatine as an absorbent.

SOIL.

ABSORPTION OF FERTILIZERS.

Selective absorption of different fertilizers by the soil was early studied by Frank [c] and by Treutler, [d] as described above.

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[a] Zeit. phys. Chem., **59,** 284 (1907).

[b] Bul. Soc. Chim., **35,** 676 (1906).

[c] Landw. Vers.-Stat., **8,** 45 (1866).

[d] Ibid., **12,** 184 (1869); **15,** 371 (1872).

PAPER.

ABSORPTION OF NEUTRAL SALTS AND DYES.

Schönbein[a] dipped strips of paper into different solutions, determined the heights to which the solution and the pure solvent rose in the paper, and observed their ratio. Since the paper absorbs the salt or organic coloring matter from solution, the higher layers are more and more dilute till near the top of the wetted paper one finds pure solvent. Göppelsröder[b] has used this selective property of paper to separate different dyes. He obtained a rose-red substance, probably fuchsine, from commercial azuline, which lost its violet tint and became a purer blue. Bayley[c] noticed that when drops of certain solutions fell on filter paper there was a separation into a water ring surrounding a solution more concentrated than the original solution. He found, too, that with increasing dilution the amount of separation became greater, and that increase in temperature and looseness of texture lowered the absorptive effect.

Lloyd[d] has determined the relative separations of different salts and finds that with sodium chloride no separation occurs, while sulphuric acid and solutions of ferric sulphate and of salts of silver, lead, and mercury suffer more or less separation into water and a stronger solution. Using the same method, Trey[e] has effected a separation of cadmium from copper. The copper cadmium solution is made alkaline with ammonia and diluted until the blue color is scarcely visible. Several drops of the solution are allowed to spread into a filter paper, and when the wet paper is subjected to ammonium sulphide vapor three rings appear—an outer water ring, which has been robbed of soluble material by the absorbing action of the paper; a yellow ring of cadmium sulphide precipitated from the soluble cadmium salt which was less strongly absorbed by the paper than the copper salt; and in the center is a black circle of mixed copper and cadmium sulphides, the copper salt being held back by the absorptive effect of the paper, while the liquid as a whole follows its normal tendency to spread, and thus the water appears to travel faster in the filter paper than the cadmium salt solution; the cadmium salt seems to spread slower than the water, but faster than the copper solution. Vriens[f] passed dilute nitric acid through several filter papers and found the absorption of acid, as shown by decrease in concentration, to be proportional to the number of filter papers used. J. J. Thomson[a] has made similar observations with filter paper. Fischer and Schmidner[b] allowed a saturated solution of ferrous ammonium sulphate to diffuse upwards through rolls of filter paper inside of a glass tube, and found that the proportion of the constituents in the filter paper was the same as in the double salt, although the absolute amounts had been diminished.

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[a] Verhandlung d. Naturforsch. Ges. in Basel, **3**, 249, (1861-63); Pogg. Ann., **114**, 275 (1861).

[b] Ibid., **3**, 263 (1861–63); Mitteil d. techn. Gewerbemuseums, Wien. (1889).

[c] Jour. Chem. Soc., **33**, 304 (1876).

[d] Chem. News, **51**, 51 (1885).

[e] Zeit. anal. Chem., **37**, 743 (1898).

[f] Zeit. phys. Chem., **31**, 230 (1899).

Cameron and Bell[c] have studied the rise of solutions and of pure solvents in paper, using aqueous solutions of malachite green, eosine, and potassium chloride, and mixtures of the two dye solutions and of eosine and potassium chloride. The rise of water and of solution is well represented by the equation $y^n = Kt$, where y is the height to which the paper is wetted, t is the time, and n and K are constants. They were able to separate the dyes from each other and from potassium chloride and showed that the presence of potassium chloride decreased markedly the height to which eosine rose in the paper in a given time.

COTTON.

ABSORPTION OF POTASH FROM POTASSIUM CHLORIDE SOLUTIONS.

These same investigators[d] wrapped strips of sensitive blue litmus paper in absorbent cotton moistened with distilled water freed from carbon dioxide and showing no reaction with a very sensitive specimen of litmus. A slight pressure was applied in order to insure intimate contact. In the course of about fifteen minutes the litmus paper had become decidedly pink, apparently showing an acid reaction. Two wads of this same cotton were placed in beakers, one containing a solution of potassium chloride neutral to litmus and the other containing potassium acetate with a slight but sufficient excess of acetic acid to redden litmus. Within a few minutes the supernatant liquor in the beaker containing potassium chloride had become distinctly acid, as shown by the further addition of litmus, while the supernatant solution in the beaker containing the acetate had become distinctly alkaline to both litmus and phenolphthalein. It is obvious, therefore, that the reddening of the litmus was a true absorption effect.

Absorbent cotton has the power of absorbing potash from a potassium chloride solution. A tube which was filled with absorbent cotton was placed in a beaker containing a solution of potassium chloride neutral to litmus. The solution after passing through the cotton was decidedly acid. But when potassium acetate was substituted for potassium chloride, even though a slight excess of acid was present, the solution after passing through the cotton was alkaline to litmus or phenolphthalein. Similar results were obtained by merely agitating wads of cotton in solutions of the reagents.

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[a] Applications of Dynamics to Physics and Chemistry (1888), p. 191.

[b] Ann. Chem. (Liebig), **272**, 156 (1893.)

[c] The Mineral Constituents of the Soil Solution, Bul. No. 30, Bureau of Soils, U. S. Dept. of Agr., (1905); Jour. Phys. Chem., **10**, 658 (1906).

[d] Bul. 30, Bureau of Soils, Dept. Agr. (1905).

BARIUM SULPHATE.

ABSORPTION OF SODA FROM SODIUM SULPHATE SOLUTION.

In another experiment a solution of sodium sulphate neutral to litmus was added to a solution of barium chloride neutral to litmus in the cold. After the precipitate subsided the supernatant solution was found to be acid. The experiment was repeated, using potassium sulphate instead of sodium sulphate, and the supernatant solution was alkaline. These experiments indicate that the barium sulphate precipitate absorbs some of the constituents of the solution, that the relative amount of acid and alkali absorbed may be varied, and that the absorbing medium may act very differently toward bases or acids.

KAOLIN.

E. C. Sullivan,[a] using magnesium and sodium chloride solutions, repeated Kohler's[b] experiments on the filtration of salt solutions through kaolin and confirmed his result that the filtrate from a neutral salt solution is slightly acid. Kohler attributed this effect to a selective concentration of dissolved substance—an adsorption of the base. But Sullivan accounts for this acidity in the filtrate by an exchange of the magnesium and sodium of these salts in part for the iron and aluminum of the kaolin, the salts of the latter metals undergoing extensive hydrolysis in dilute solution. The acidity observed is of the same order of magnitude as the quantity of trivalent bases found in dilute copper sulphate solution after contact with kaolin. He further suggests that the acidity of a salt solution after filtration through a substance, such as kaolin, through which the liquid diffuses but slowly, may be due to some extent to the greater velocity of diffusion of the acid constituent of the salt, which is present owing to hydrolysis, while the base is present (for salts of heavy metals) to a greater or less extent in the colloidal condition and colloids are marked by their very slow rate of diffusion.

COPPER HYDROXIDE.

Tommasi[c] found that the solutions of such neutral salts as sodium chloride and sulphate and potassium chloride and bromide become basic when precipitated copper hydroxide is added to the solution. The acid is absorbed by the copper hydroxide, which then becomes green in color.

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[a] The Interaction Between Minerals and Water Solutions, Bul. 312, U. S. Geol. Survey, p. 8, 1907.

[b] Zeit. prakt. Geol., **11**, 49 (1903).

[c] Compt. rend., **92**, 453 (1881).

NEGATIVE ABSORPTION.

CHARCOAL.

Lagergren[a] found that either solvent or solute could be absorbed, or, in other words, that the solution could become more concentrated or less concentrated. Thus solutions of sodium chloride, potassium chloride, ammonium chloride, and ammonium bromide became more concentrated after contact with charcoal, while sodium nitrate, potassium nitrate, sodium sulphate, potassium sulphate, and ammonium nitrate become less concentrated. This author states that he could find no evidence of any change in alkalinity or acidity of the solutions. This behavior has been ascribed by the author to an increase in the density at the surface of the solid—an increase in density which involves an increase in pressure. If, therefore, an increase of pressure increases the solubility, or, in other words, if solubility is accompanied by a decrease of volume, there will be a positive absorption; but under reverse conditions there will be a negative absorption. Lagergren has calculated the degree of absorption from the surface of the solid exposed, the radius of molecular action, and the density of water under different pressures. The results of the calculation for absorption of ammonium chloride and the observed absorption agree fairly well.

KAOLIN AND GLASS WOOL.

Parallel results have been obtained where the absorbing material is kaolin and glass wool, the negative absorption of sodium chloride by kaolin having been found by van Bemmelen.[b]

CLAY.

White china clay has been used as an absorbing medium by Cushman,[c] who finds a considerable decrease in the basic ions from solutions of ammonium chloride, barium chloride, and aluminum sulphate. The data indicate that there may have been also a negative absorption of the sulphuric acid, i. e., a considerable absorption of water from aluminum sulphate solutions, which then became more concentrated with sulphuric acid, although the author thinks the phenomenon is due entirely to the fact that, owing to hydrolysis, free acid necessarily exists in a solution of a salt of a trivalent base.

SELECTIVE ABSORPTION OF DYES.

Dyes forming colloidal solutions are extremely sensitive to electrolytes in regard to their adsorption[d], the effect being proportional to the size of the colloidal particles. In the case of electro-negative dyes (Congo-red) cations facilitate absorption, anions depress it; with electro-positive dyes (toluidine-blue) the opposite is seen, but in both cases the effect of anions is small. Salts of the heavy metals which form positively charged colloidal hydroxides powerfully promote adsorption of Congo-red. The facilitating ion is carried down with the dye. The presence of a stable colloid, such as gelatine, protects Congo-red from the action of electrolytes. When gelatine is precipitated by tannin, its adsorbed electrolytes are split off. In the process of blood-clotting there is a diminution of electrical conductivity, ions (probably of calcium) disappearing from solution. There is no evidence of a sudden separation of electrolytes in the tissues at the moment of death, although there is a gradual one when a living tissue is warmed from 11° to 56°. In the action of rennet on milk there is a slight increase in conductivity, an additional fact showing this process to be quite different from blood-clotting. In all probability rennet action is only an expression of pepsin action in neutral or faintly alkaline media (Pawloff).

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[a] Bihang till K. Sv. Vet. Akad. Handl., **24**, Afd. II. No. 4 (1898).

[b] Zeit. anorg. Chem., **23**, 321 (1900).

[c] Bul. No. 92, Bureau of Chemistry, U. S. Dept. Agr., 1905, p. 18.

[d] Bayliss, Biochem. Jour., **1**, 175 (1906).

Recently Craw[a] has studied the filtration of crystalloids and colloids through Martin's gelatine filter (a Pasteur-Chamberland filter the pores of which are filled with solid gelatine) and finds it highly but not completely permeable for such crystalloids as sodium chloride, potassium iodide, and butyric acid. The work of Waymouth Reid showing that this filter is slightly permeable to colloids was confirmed. As filtration proceeds the crystalloids show an increasing concentration in the filtrate, whereas the colloids gradually decrease to zero and are completely retained by the filter. The presence of one substance in solution often affects the rate of filtration of another. The permeability depends, too, upon the gelatine used. Thus a filter prepared with 15 per cent gelatine solution is less permeable to certain colloids than a filter prepared with 7.5 per cent gelatine solution, and formalized gelatine is less permeable to sodium chloride than ordinary gelatine.

APPLICATION OF SELECTIVE ABSORPTION IN PHYSIOLOGY.

The theories of absorption have been applied to physiology in a research on the neutralization by lysin and by antilysin and on diffusion through gelatine filters.[b]

SELECTIVE ABSORPTION OF DYES BY SOILS.

Sjollema[c] found that different solid soil constituents have very different absorptive power for dyes. He classifies as colloids those substances which are colored by organic dyes, and thus excludes undecomposed mineral fragments and quartz which are not tinted by the dyes he used. The definition of a colloid thus implied is so inclusive as to bring such substances as carbon black, platinum black, and all other amorphous substances, as well as powdered crystalline substances, under the head of colloids, and consequently it becomes meaningless. It has been shown[a] by Cameron and Patten that gentian violet (*gentianin*) is adsorbed by quartz to a considerable extent, and this same dye colors other soil grains, crystalline as well as amorphous.

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[a] Proc. Roy. Soc., B **77**, 311 (1906).

[b] Craw. Zeit. phys. Chem., **52**, 585 (1905).

[c] Jour. f. Landw., **53**, 67 (1905).

Cameron and Bell[b] found that solutions of dyes poured through soils always yield clear water for the first runnings. When eosin solution is used the dye soon appears in the percolate, but soils retain methylene blue, malachite green, gentian violet, and some other dyes with remarkable tenacity. Separations of a mixture of eosin and methylene blue were made by percolation, the methylene blue being completely retained by the soil, while the eosin was comparatively readily removed by washing. It was shown, too, that for any particular solution of a dye the various soils had a definite absorption limit; that is, if the solution is poured on a given mass of soil slowly and at a very uniform rate there is a point at which the soil will cease to absorb the dye, and the solution will come through unchanged. Fairly good duplicate determinations for the absorptive power of any particular soil can be made in this way. Heavy soils absorb generally more than light soils, and black, red, or dark-brown soils more than those of lighter color. The presence of humus adds very considerably to the absorptive power of a soil. In some cases, at least, the absorption of one dye by a soil does not materially reduce its capacity for retaining a second dye. It was found, too, that while a dye might be so firmly held by a soil as to resist removal on leaching, the soil nevertheless gave up dye to filter paper and to some kinds of blotting paper. Likewise, absorbed dye may be removed unchanged in some instances by use of a different solvent—for example, alcohol—when further leaching with water is practically of no avail. These authors state that, in general, papers are better absorbents for dyes than soils, but, on the other hand, some solutes, such as alkalies, are generally absorbed more powerfully by soils than by papers. This has an important bearing on the common practice of testing the reaction of a soil with moist litmus paper. Blue litmus, as is well known, is the sodium salt of the red dye. In aqueous solution it must be considerably hydrolized, so that when a paper saturated with it is brought into intimate contact with a soil the base is absorbed more readily by the soil and the remaining acid more readily by the paper, with the consequence that the latter becomes red. This explanation of the reddening of litmus paper by soils was confirmed by other experiments.

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[a] Jour. Phys. Chem., **11**, 581 (1907); Trans. Am. Electrochem. Soc., **10**, 67 (1906).

[b] The Mineral Constituents of the Soil, Bul. 30, Bureau of Soils, U. S. Dept. of Agr , 1905, p. 57.

SELECTIVE ABSORPTION AND THE ACIDITY TEST FOR SOILS.

Cameron and Bell further suggest that it might be argued from these experiments that the only test as to the presence of an acid in a soil is the formation of an acid solution when extracted with water. It is true that this is the only satisfactory criterion which suggests itself. As the experiments just cited show, solid and other absorbent substances can and do absorb acids, some more than others, and it is quite possible that an absorbed acid, which was not easily removed from a soil by water, might be removed by paper, if paper were the better absorber for that particular acid. It is well, therefore, to view with caution the prevalent notions as to the wide distribution of acid soils founded on a very uncertain criterion, and especially in view of the fact that the great majority of soils yield aqueous extracts which on heating in platinum, show alkaline reactions. Most of our field crops can withstand a fairly high concentration of acid; but clover[a] is especially sensitive, being inhibited in growth by concentrations less than twenty-thousandth normal (N/20,000). Yet cases have been observed where clover was found growing well in soils apparently very acid, the true explanation being undoubtedly that the supposed estimation of acidity was, in fact, a measurement of the absorptive capacity of the soil.

Furthermore, it is probably fallacious to assume that the acidity of a soil can be estimated by adding calcium hydrate, ammonia, or other alkalies in solution until the soil will turn red litmus paper blue when the paper is brought into contact with the soil, since it has been clearly shown that most soils absorb these substances much more effectively than does litmus paper. If these solutions be added to the soil slowly (for absorption is not an instantaneous process, but requires appreciable time to attain equilibrium), it frequently is astonishing how much alkali can be taken up before an alkaline reaction can be detected by the test paper—a fact repeatedly observed by various investigators, but the significance of which had not hitherto been recognized.

GENERAL STATEMENT CONCERNING SELECTIVE ABSORPTION BY SOILS.

Regarding the degree to which the different constituents of the soil solution are absorbed, several generalizations can be made; but from the foregoing data and discussion it will be evident that each soil will exert its own peculiar effect in retaining soluble matter, and that, while we may seek to classify a fertilizer as adding potassium or nitrates or phosphates to the soil, the *form* or *salt* in which the fertilizer is added will affect its absorption by soil.

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[a] Cameron and Breazeale, Jour. Phys. Chem., 8, 1 (1904).

Of the basic radicals, potassium is most strongly bound by the soil. If a soil is saturated with potassium, then one may replace the more recently absorbed potassium by other bases merely by treating the soil repeatedly with a solution of another solute, for the potassium is distributed each time between the soil and solution, and of course when the solution is removed from contact with the soil the potassium is withdrawn, too, and can exercise no further effect upon the equilibrium. Meanwhile the soil is absorbing the base or bases in these solutions applied to the soil to remove potassium. In effect we have replaced potassium by another base or bases; but it by no means follows that we may have here a case of chemical exchange by a rearrangement of definite compounds, especially as the replacement need not follow the chemical equivalence of the bases involved. This predominant retention of potassium by soils is undoubtedly the main reason why potassium is so little in evidence among the soluble salts of alkali soils—salts which have come up through the lower layers of soil and finally been concentrated near the surface, sodium and calcium salts passing on up to the surface, and, to a less extent, the magnesium salts also. It is true that in general the magnesium silicates are quite readily soluble and much hydrolyzed by water, but magnesium is absorbed to a much greater extent than calcium or sodium, although to a lesser extent than potassium.

ABSORPTION FROM VARIOUS SOLVENTS.

PICRIC ACID IN WATER, ALCOHOL, AND BENZENE.

The experiments by Walker and Appleyard[a] on absorption by silk have shown that while picric acid is absorbed by silk from solutions in water and alcohol, yet in benzene solution there was no absorption. The nature of the solvent plays, therefore, an important rôle. The relative solubilities of picric acid in the three solvents do not throw any light on the absorptive power from the different solvents, for the solubility of picric acid in benzene lies between the solubility in water and that in alcohol.

DYES IN PETROLEUM, BENZENE, XYLENE, CARBON TETRACHLORIDE, AND CARBON DISULPHIDE.

Tsvett[b] has shown that many dyes dissolved in light petroleum, benzene, xylene, carbon tetrachloride, or carbon disulphide are precipitated by powdered substances, from which they may be extracted by alcohol, ether, acetone, or chloroform. There is further an adsorption series in which the substances can replace each other on the absorbent. When a mixed solution, as, for instance, chlorophyll dissolved in carbon disulphide, is filtered through a column of precipitated calcium carbonate, the dyes are precipitated, but mutually replace each other and arrange themselves according to the adsorption series in the direction of the stream. If any zone is not pure, it can be extracted and the adsorption repeated until the desired degree of purity is attained.

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[a] Jour. Chem. Soc., **69**, 1334 (1896).

[b] Chem. Centr., 1906, ii, 1286; from Ber. deutsch. bot. Ges., **24**, 384–393.

MAGNITUDE OF ABSORPTION IN DIFFERENT SOLVENTS.

Rosenthaler and Türk,[a] in studying the effect of the solvent upon the degree of absorption, found that it is greatest from aqueous solutions. The absorption is less from solutions in ethyl alcohol, methyl alcohol, ethyl acetate, acetone, and chloroform, in the order named.

Freundlich, in his recent paper on absorption, has compared the absorption for a number of different solvents, and for dilute solution it appears to have the same order of magnitude in all of the different solvents; but, while in the same order of magnitude, there are really differences, which become more pronounced as the concentration increases, and are widely different in strong solutions.

DISTRIBUTION.

The earlier investigators appear to have had no true conception of the distribution of a substance between the liquid and solid material. Salomon[b] agrees with Liebig that absorption is purely physical in nature, but does not consider the concentration of the end solution left above the solid.

Biedermann[c] also plots as abscissa the quantity of soil per hundred parts of solution and as ordinate the percentage of solute absorbed from solution. This is a very useful and practical method of representing results, but fails to give a clear idea of the phenomena of distribution, which is tacitly assumed in Biedermann's work.

POTASSIUM BETWEEN SOIL AND SOLUTION.

Peters's[d] results on the absorption of potassium chloride by a soil have been recalculated in Table III to show the quantities of potassium in unit quantities of a solution and a soil. He neglected, however, the chlorine; but it is altogether likely that less of it would have been found absorbed than corresponds with the absorbed potassium. It is safe, therefore, to assume that Peters's analytical data give a representative distribution curve for the basic radical potassium between a soil and water. To bring out more clearly the enormous effect exercised by the soil in withdrawing soluble material from solution, the percentage of potassium absorbed by the soil from solution is given for each concentration in the accompanying table. It will be seen that this absorptive effect is nearly twice as great with dilute solution as in the strongest solution used, varying from 94 per cent of the total potassium present in the dilute solution to 54.9 per cent for a solution 20 times stronger.

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[a] Arch. Pharm., **244**, 517 (1906).

[b] Landw. Vers.-Stat., **9**, 351 (1867).

[c] Landw. Vers.-Stat., **11**, 1 (1869).

[d] Landw. Vers.-Stat., **2**, 129 (1860).

TABLE III.—*Distribution of potassium between soil and solution of potassium chloride, according to Peters.*

Potassium per kilo soil.	Potassium per liter of solution.	Total potassium present absorbed by soil.	Potassium per kilo soil.	Potassium per liter of solution.	Total potassium present absorbed by soil.
Grams.	*Gram.*	*Per cent.*	*Grams.*	*Grams.*	*Per cent.*
1.011	0.0648	94.0	1.390	0.127	91.6
1.096	.0628	94.5	1.453	.203	87.9
1.168	.0677	89.2	1.511	.361	80.7
1.238	.0797	94.0	1.579	.679	70.3
1.328	.089	93.8	1.610	1.310	54.9

CALCIUM BETWEEN SOIL AND SOLUTION.

Peters has also determined the quantity of calcium extracted from the soil by the same solutions which were being studied with respect to the absorption of potassium. He found that calcium is distributed in a manner nearly analogous to potassium, and that the curve for the distribution of calcium between soil and water has apparently the same general form as that for potassium. This observation indicates that the absorption of two solutes may proceed almost independently of each other, at least when the concentrations of both are low.

HYDROCHLORIC ACID BETWEEN CARBON BLACK AND SOLUTION.

When carbon black is shaken with an aqueous solution of hydrochloric acid, Kelberin[a] found that there is a perfectly definite distribution ratio; the results could be duplicated to within a fraction of 1 per cent.

INCONSTANCY OF DISTRIBUTION RATIO.

Kroeker[b] studied the relation between absorption and time of contact, quantity of carbon, and concentration of solution, and found that the distribution ratio between carbon and solution is not constant, but that relatively more is absorbed from dilute solutions than from strong. Schmidt[c], using Van Bemmelen's data[d] has sought to show that the distribution ratio of potassium sulphate, potassium nitrate, potassium chloride, sulphuric acid, hydrochloric acid, and nitric acid was constant. This result has been contested by Van Bemmelen,[a] who points out that the distribution ratio of a substance between solid and liquid need not necessarily be constant in the case of equilibrium between solid and liquid solutions.

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[a] See Ostwald, Lehrbuch der allgemeine Chemie (1891), p. 1096.

[b] Über die Adsorption gelöster Körper durch Kohle, Dis., Berlin (1892).

[c] Zeit. phys. Chem., **15,** 56 (1894).

[d] Jour. prakt. Chem., **131,** 324 (1881).

DISTRIBUTION FORMULAS.

A number of investigators[b] have advanced formulas to express the distribution of a solute between a solvent and an absorbing medium. These expressions have been generally suggested by the apparent analogy to the distribution of the solute between two immiscible solvents, for which two general equations have been proposed.

If c be the concentration of the solute in one solvent and c_1 the concentration of the other, then when there is no association of solute in either solvent the distribution is described by the formula $c/c_1 = K$; but if there be association of solute in either solvent, the formula becomes $\frac{c^n}{c_1} = K$. K is a constant for any standard conditions of temperature.

Ostwald[c] has proposed this same form of equation slightly modified, $x/m = \alpha\, C^{\frac{1}{p}}$, where x is the total mass of solute absorbed and m is the mass of the absorbent; C is the concentration of the solution, and p and α are constants.

This exponential formula has been found to hold more or less well for a number of cases of absorption, of which a few will be cited. Thus Schmidt[d] found it held for the absorption of iodine and several acids by charcoal, but it did not hold for the absorption of picric acid by cellulose or of eosine or malachite green by silk. Küster[e] found such a relation held for the absorption of iodine by starch.

Walker and Appleyard[f] have studied a case of unusual interest. They found that the distribution of picric acid between water and silk was described by the formula $\frac{S}{W^{\frac{1}{2.7}}} = 35.5$, where S represented concentration of the dye in the silk and W the concentration in water. This would indicate that at the concentration studied the molecule of picric acid in the water solution is 2.7 times as large as that represented by the formula $C_6H_2(NO_2)_3OH$, at least; but this is negatived by the cryoscopic measurements of the osmotic pressure and of the conductivities of aqueous solutions of picric acid.

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[a] Zeit. phys. Chem., **18**, 331 (1895).

[b] Schmidt, Zeit. phys. Chem., **15**, 60 (1894); Küster, Annalen, **283**, 360 (1894); Walker and Appleyard, Jour. Chem. Soc., **69**, 1334 (1896); Biltz, Ber. deutsch. chem. Ges., **37**, 1766 (1900); **38**, 2963, 2973, 4143 (1905); Zacharias, Zeit. phys. Chem., **39**, 468 (1901).

[c] Lehrbuch der Allgemeine Chemie II. (2 Aufl.), 232.

[d] Zeit. phys. Chem., **15**, 60 (1894).

[e] Annalen, **283**, 360 (1894).

[f] Jour. Chem. Soc., **69**, 1334 (1896).

Biltz[a] has studied several similar cases. An especially interesting one is the absorption of alizarin by ferric oxide, the distribution being described by an exponential formula, but the curve representing it not going through the origin. That is, the concentration of the solution must be above a certain value before any absorption on the solid can take place. Similar cases, as, for instance, in the absorption of phosphates from solution by soils, have been observed in this laboratory.

Freundlich[b] has added to Ostwald's equation the concept that the total quantity of solute present in the system has an effect upon the equilibrium—though the explanation for this is not yet at hand—and his empirical equation, derived from Ostwald's, takes the form $\lambda = \frac{V}{m} ln\left(\frac{a}{a-x}\right)$, where λ is a constant, V is the volume of solution, m the mass of absorbent, a the total solute in the system, and x the total quantity of solute obsorbed. Freundlich restricts this formula to dilute solutions and finds that it does not hold for solutions which conduct electricity well.

Travers[c] objects to Freundlich's statement that adsorption is independent of the solid adsorbent, the solute, or the solvent used, and, in addition, makes the point that a rigid distinction between crystalline solid solutions and highly viscous liquid solutions, such as glass, should be made. According to Travers, many cases of absorption which Freundlich would class as purely adsorption effects are in reality highly viscous liquid solutions formed at the surface of the adsorbing solid.

Freundlich[d] in his answer to Travers states that he has not thought that the *magnitude* of the adsorption effect is independent of the solid adsorbent, the solute, and the solvent, but merely that the same solid adsorbs different solutes from solution in the same relative quantities from different solvents.

Travers also takes exception to Freundlich's statement that the magnitude of adsorption is independent of the temperature. Freundlich admits that, broadly speaking, Travers's criticism is justified. Freundlich means merely to indicate that the temperature effect is so slight as to render unnecessary the use of a thermostat in the measurements made by himself.

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[a] Ber. deutsch. chem. Ges., **37**, 1766, 3138 (1904); **38**, 2963, 2973, 4143 (1905). Nach. K. Ges. Wiss. Göttingen, Math.-Phys. Klasse, **1**, 1 (1904); **1**, 1 (1905); **3**, 1 (1905), with Kurt Utescher.

[b] Zeit. phys. Chem., **57**, 385 (1906).

[c] Zeit. Phys. Chem., **61**, 241 (1907).

[d] Zeit. Phys. Chem., **61**, 249 (1907).

Hedin[a] has shown that charcoal absorbs trypsin almost completely from dilute solution, and as the concentration of trypsin increases the charcoal gradually becomes saturated. Arguing from Freundlich's[b] treatment of adsorption, Hedin concludes that this behavior of trypsin is different from that of adsorbed crystalloids, in that the trypsin shows a specific attraction for the charcoal, the first portions adsorbed being so strongly bound as to suggest an irreversible process. But in reality Hedin's observation with trypsin agrees with numerous systems where the adsorbed solute is a crystalloid.[c]

SULPHURIC AND HYDROCHLORIC ACIDS BETWEEN TEXTILES AND SOLUTIONS.

Vignon and Mollard[d] have shown the distribution of sulphuric and of hydrochloric acids between their respective aqueous solutions and the textiles unbleached silk, ungummed silk (soire décreusée), cotton, and linen. They find that cotton does not absorb these acids, but silk and linen take up relatively more acid from dilute than from concentrated solution, the coefficient of distribution $\frac{C_2}{C_1}$ increasing greatly as the acids are diluted, and decreasing slightly with rise in temperature. Equilibrium is established within one hour in those systems where the strength of acid was in round numbers from 1 per cent to 0.1 per cent. From 100 c. c. to 400 c. c. of solution was maintained in contact with 10 grams of the textile absorbent. This research establishes the fact of distribution in these systems, but the data is insufficient to give the function $\phi\ (C_2) = C_1$, even approximately.[e]

SALTS BETWEEN GELATINE AND SOLUTION.

Bayliss[f] has found that the curve of electrical conductivity of successive distilled water extracts of gelatine is a hyperbola. It is therefore impossible to wash out all the electrolytes except by an infinite number of changes of distilled water, each change removing a less percentage than the previous one; in other words, the electrolytes are present in an absorbed form. When the gelatine is washed nearly free from such admixtures and is placed in solutions of electrolytes, it again absorbs them, and so the conductivity of the solution is diminished. But it must not be taken as established that an absorbed solute is unable to contribute to the electrical conductivity of the system in which it exists. It has been shown by Patten[a] that soil grains which have absorbed alkali carbonates, when in aqueous suspension, add very greatly to the electrical conductivity, and when removed by centrifuging take with them the adsorbed or absorbed material, leaving the supernatant solution lower in conductivity than before. Similarly soils made up to paste with water or salt solution show an electrical conductivity due in part to salt which is adsorbed (or absorbed) and is very resistant to removal by leaching.[b]

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[a] Hoppe-Seyler's Zeit. physiol. Chem., 5, 504 (1907); see also Hedin, Bio.-Chem. Jour., 2. Biltz, Zeit. phys. Chem., **47**, 615 (1904); Nernst, Zeit. Elektrochem., **10**, 377 (1904); Craw, Zeit. phys. Chem., **52**, 569 (1905).

[b] Zeit. phys. Chem., **57**, 385 (1906).

[c] Freundlich's restriction of the validity of his formula to *dilute solution* and to *solutes which do not yield conducting solutions* tacitly admits the very point Hedin is making, i. e., that adsorption is a specific effect which depends *primarily* upon the composition of the adsorbent, of the solute, and of the solvent. The lowering or raising of the surface tension, *solid-liquid*, upon which Freundlich bases his treatment, is controlled by the composition of the solid and of the liquid which constitute the liquid-solid surface.

[d] Bul. Soc. Chim. (3), **36**, 1304 (1906); Compt. rend., **143**, 550 (1906); see also Knecht, Rawson, Löwenthal, Handbuch der Färbung von Spinnfasern.

[e] See also Vignon, Bul. Soc. Chim. (4), **1**, **2**, 273 (1907) on the relation of the electrical conductivity of the dye solution to its efficiency in coloring.

[f] Bio.-Chem. Jour., **1**, 175 (1906).

FERRIC CHLORIDE BETWEEN FERRIC HYDROXIDE AND SOLUTION.

Duclaux[c] opposes the contention of Nicolardot and Wyrouboff that the formation of a compound $Fe_2(OH)_6 \frac{1}{150} Fe_2Cl_6$ limits the possibility of removing chloride from colloidal ferric hydroxide. Duclaux has obtained by dialysis a ferric hydroxide containing less than one-third of the amount of chloride implied by the above formula, and sees no reason why the removal of chloride should not be carried further.

DEFINITIONS.

MAXIMUM ABSORPTIVE CAPACITY.

The maximum amount of a solute which an absorbent may remove from solution is, under any standard conditions of temperature, a perfectly definite quantity, characteristic of the absorbent, and is a measure of what may be defined as the "maximum absorptive capacity" of an absorbent. This maximum amount of solute can not, however, be absorbed from a solution of any concentration whatever, as is shown by equilibrium experiments,[d] but only from a solution which is saturated with respect to the solute and at the same time in equilibrium with the absorbent. Practically this case could only be realized when some of the solute is present as a solid phase, and such a system has generally but little interest, owing to the difficulty of distinguishing between the absorbed and nonabsorbed solid. It is, therefore, more convenient to estimate the maximum absorptive capacity of an absorbent by extrapolating from data obtained with solutions somewhat below saturation.

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[a] Electrochem. and Met. Ind. **5**, 257 (1907).

[b] Whitney and Means, Division of Soils, U. S. Dept. Agr., Bul. 8, 1897.

[c] Compt. rend. **143**, 296 (1906).

[d] Cameron and Bell, Bul. No. 30, Bureau of Soils, U. S. Dept. Agr. 1905; Schreiner and Failyer, Bul. No. 32, Bureau of Soils, U. S. Dept. Agr. 1906; Patten, Trans. Am. Electrochem. Soc., **10**, 67 (1906).

SPECIFIC ABSORPTIVE CAPACITY.

From a solution containing less solute than is required to saturate it an absorbent can remove a quantity less than that which measures its maximum absorptive capacity, but a quantity which is nevertheless perfectly definite for any given concentration of solution. This quantity may be defined as the specific absorption with respect to that particular solution.

Thus a solution of potassium chloride containing 500 parts per million of potassium chloride when brought into contact with a soil will lose potassium chloride, as the soil absorbs it, at a speed which gradually decreases till the salt reaches a final distribution between soil and solution. The weight of potassium chloride absorbed at a given temperature by 1 gram of soil represents the specific absorptive capacity of the soil for that particular salt at that particular concentration of the salt. This concentration is not the original concentration of solution—500 parts per million of potassium chloride—but is the final concentration reached after the absorption has been completed. If by a slight alteration of other conditions, such as temperature, the soil absorbs temporarily more salt than when the chosen temperature is again reached, the solution will remove the excess of absorbed salt from the soil and reduce the quantity of potassium chloride remaining in the soil to its absorptive capacity for the original conditions. In other words, absorption is a reversible phenomenon.

GENTIAN VIOLET DYE BETWEEN SOIL AND SOLUTION.

It is significant that those substances which are prominent as fertilizer constituents, namely, potassium, calcium, ammonia, phosphoric acid, and proteid organic matter, are substances which are markedly absorbed by soils. From the increasing knowledge of the effect of adsorbing surfaces upon the chemical reactions which might ordinarily be expected to take place among these various soil constituents, it is evident that such reactions may be and probably are very much modified when they take place in the presence of the adsorbing surfaces. In studying the distribution of an added solute between a soil and water there is difficulty in obtaining complete data when the soil already contains the solute in question. There is no method of determining absolutely the quantity of any soluble material in a soil which has already been absorbed on the soil grains, and even though the amount of solute present in the water added to the soil be measured exactly, the total amount present as absorbed material can not be ascertained.

To determine the character of this distribution more readily, water-soluble bodies have been used which are not contained in the soil naturally, and which are not appreciably changed by contact with the soil. Thus there are known the quantities of solute, of the soil, and of the water, and by varying the weight of solute a series of systems in equilibrium are obtained and the distribution of solute between water and soil can be examined quantitatively. When the character of the distribution is thus determined, a criterion is obtained for comparison with the less exact data of the distribution observed with soluble bodies which commonly exist in the soil, such as potassium salts, nitrates, phosphates, or water-soluble organic matter. Similar equilibrium experiments were made using fine quartz flour instead of soil to eliminate the effect of (1) the soluble material already present in the soil and (2) of the organic matter in the soil, which latter exerts so large an absorbing effect upon the solute as to mask the distribution of this solute between the mineral components of the soil and the solution.

The dye gentian violet has been found particularly well adapted to studying distribution, because it is changed very slightly, if at all, by contact with the soils used or with quartz flour, and because it can be readily estimated colorimetrically to within a fraction of a part in a million of solution. It is a basic dye (gentianin), represented by the formula $(CH_3)_2N.C_6H_3:SCl.N:C_6H_3.NH_2$, and is analogous in that respect to ammonia bases in general and to some fermented manures. The sample of gentian violet used gave characteristic reactions, viz: (1) Dilute aqueous acids, as hydrochloric or nitric acids, turn the aqueous dye from a violet to green; (2) concentrated sulphuric acid dissolves the dye, forming a yellowish-green solution, and (3) aqueous sodium hydroxide gives a violet color. The solubility of gentian violet in water at 25° C. was found to be 6.81 per cent of solution by weight. The experiments were carried out at room temperature which varied but little from 25° C.

One hundred gram portions of each soil were placed in strong glass bottles of some 225 c. c. capacity, with 150 c. c. of dye solution, agitated in a shaker for several days, placed in a centrifuge and whirled for several hours, and a small portion of the liquid withdrawn from each and the dye content estimated colorimetrically. The bottles were then replaced in the shaker, again centrifuged, and the dye in solution again determined. This was repeated till equilibrium had been reached, which usually required about a week's time.

By a separate experiment it was found that 100 grams Marshall silt loam absorb 4 c.c. of water from a saturated atmosphere at 29° C. This was taken as representing the volume of water which is extracted from the solution when brought into contact with this soil. So, in effect, the volume of solution for which the concentration of dye is determined is not 150 c.c.—the volume of liquid added—but 146 c.c. Similarly, 100 grams Hagerstown loam absorbs 4.5 c.c. of water from a saturated atmosphere at 29° C., and accordingly this value was used in calculating the concentration of the solutions after absorption. The quartz flour used absorbed 0.8 c.c. water under the same conditions; but as this correction affects the distribution curve by less than 1 per cent, it is neglected.

Table IV gives the experimental data for the distribution of gentian violet between soil and water. The first column shows the total quantity of dye added; the weight of dye withdrawn from solution per kilo of soil is shown in the second column for Marshall silt loam, a representative fertile soil, and the grams of dye remaining in a liter of solution in the third column. The distribution for Hagerstown loam, another fertile soil, is given similarly in the fourth and fifth columns, and for fine quartz flour in the sixth and seventh columns.

Table IV.—*The distribution of gentian violet between soils and solution.*

[100 grams soil and 150 c.c. solution.]

Dye added.	Distribution.					
	Marshall silt loam.		Hagerstown loam.		Quartz flour.	
	Dye per kilo soil.	Dye per liter solution.	Dye per kilo soil.	Dye per liter solution.	Dye per kilo soil.	Dye per liter solution.
Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*
0.005	....	....	....	....	0.06	Trace.
.015	....	....	....	....	.14	0.0001
.075	....	....	....	....	.743	.0040
.100	....	....	....	....	.984	.0108
.200	....	....	1.9996	0.00023	1.901	.066
.300	3.00	Trace.	....	....	2.66	.224
.40	....	....	3.9998	.00140	2.89	.740
.50	4.85	0.0001	4.9996	.00250	2.95	1.370
.70	....	....	....	....	2.97	2.668
1.00	9.999	.00083	9.9825	.0120	2.93	4.710
1.50	....	....	14.95	.0325	....	....
2.00	19.99	.006	19.817	.1250	....	....
2.50	24.97	.020	....	....	2.90	14.75
3.00	29.91	.060	20.45	6.525	....	....
3.20	31.89	.070	....	....	....	....
4.00	37.00	2.050	20.25	13.500	....	....

When the concentration of the dye left in solution is taken as abscissa and the concentration in soil as ordinate, curves resembling the parabola are obtained. By extrapolating these curves the maximum absorptive capacity of the soil for gentian violet may be found: Marshall silt loam, 38 grams dye per kilo of soil; Hagerstown loam, 20.45 grams dye per kilo; quartz flour, 2.97 grams dye per kilo. The absorption capacities are in the ratio 113: 61: 1, and show that each soil has its own absorptive capacity. The soil grain area of Marshall silt loam is very nearly the same as that of Hagerstown loam when calculated on the basis of their mechanical analysis, and yet the Marshall soil absorbs nearly twice the quantity of dye taken up by the Hagerstown soil. Again, both of these soils have an area presented by their grains nearly twice as great as the surface offered by the same weight of the quartz flour used, and yet the quartz has by no means half the absorptive capacity of either of the soils. The presence of organic matter is undoubtedly a very important factor in determining the magnitude of the absorption; but this absorption of dye by quartz shows that the mineral constituents of a soil, as well as the organic matter it contains, enter in to determine its absorptive capacity. It is certain, moreover, that mineral constituents other than gelatinized products of hydrolysis are capable of absorbing soluble bodies from the soil solution to a marked extent.

Considering the concentrations of dye when the soil has nearly reached its maximum absorptive capacity, it will be seen in Table IV that Marshall silt loam abstracted from solution 92.5 per cent of the total dye added; the Hagerstown loam, 51.1 per cent; and the quartz flour, 59 per cent. At lower concentrations of dye in solution the soils absorbed relatively more dye, and although the dye is truly distributed between soil and solution the soil holds so large a portion of dye that for practical purposes the dye is all absorbed. Thus for 0.5 gram dye added the Marshall silt loam absorbed 97 per cent; the Hagerstown loam, 99.99 per cent; and the quartz flour, 59 per cent of the dye. When only 0.075 gram dye is added, the quartz flour absorbs 99 per cent, leaving only 1 per cent in solution. Consequently it is clear that absorption experiments carried on over a limited range of concentrations may lead to false conclusions regarding the distribution. These experiments further emphasize the fact that a soil may hold a relatively large quantity of water-soluble material even in contact with a very dilute aqueous solution.

EOSINE DYE BETWEEN QUARTZ FLOUR AND SOLUTION.

Table V gives the data for the distribution of sodium eosine between quartz flour and water. Here the absorptive capacity of the quartz for eosine does not tend to a limiting value—at these concentrations—as it does for gentian violet, but the absorption of eosine is nearly proportional to the quantity of eosine in solution, the distribution curve being not quite a straight line. Examples of linear distribution are known. For instance, Gaubert[a] observed it for the absorption of methylene blue by crystals of phthalic acid deposited from solution in the dye when the solution is cooled, and for the absorption of the same dye by crystals of nitrate of urea. And Van Bemmelen[b] has given an interesting case in the absorption of potassium chloride by stannic oxide.

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[a] Compt. rend., **142**, 936 (1906).

[b] Zeit. anorg. Chem., **23**, 113 (1900).

TABLE V.—*Distribution of eosine between quartz flour and solution.*

[50 grams quartz and 75 c. c. solution.]

Dye added.	Distribution.		Dye added.	Distribution.	
	Dye absorbed per kilo quartz.	Dye per liter of solution.		Dye absorbed per kilo quartz.	Dye per liter of solution.
Gram.	*Gram.*	*Gram.*	*Gram.*	*Grams.*	*Grams.*
0.00242	0.009	0.027	0.075	0.348	0.768
.0075	.0135	.091	.75	4.2	7.200
.0248	.085	.274			

MANURE EXTRACT BETWEEN SOIL AND SOLUTION.

To study the absorption of the soluble organic bodies in manures, several concentrations of a well fermented and matured extract were allowed to stand in contact with soils, with frequent shaking, for two weeks at room temperature, 25° C. Then the supernatant liquid was poured off, centrifuged, evaporated to dryness in a steam bath, then in a water oven, and weighed; ignited, weighed, and the organic matter gotten by difference. The quantity of organic matter in the original manure-extract solution was determined similarly.

TABLE VI.—*Distribution of manure extract between soil and solution.*

[500 grams soil and 2,000 c. c. solution.]

Organic matter in added extract.	Hagerstown loam.		Marshall silt loam.		Norfolk sand.	
	Organic matter absorbed per kilo soil.	Organic matter per liter solution.	Organic matter absorbed per kilo soil.	Organic matter per liter solution.	Organic matter absorbed per kilo soil.	Organic matter per liter solution.
Grams.	*Grams.*	*Gram.*	*Gram.*	*Gram.*	*Gram.*	*Grams.*
0.2940	0.058	0.133	....	....	−0.129	0.1792
.5880	.366	.203	−0.109	0.321	− .100	.3192
1.176	.721	.403	.354	.500	.077	.5687
2.350	1.180	.880	.885	.954	.440	1.0650

Table VI contains data for Hagerstown loam, Marshall silt loam, and Norfolk sand. A correction for the volume of water absorbed on the soil grains was rejected here, as it amounts to less than 1 per cent, and the data serve to show the general trend of the distribution. As there is some organic matter already present in the soil, the absorption appears negative for low concentrations of manure extract, since the organic matter comes out of the soil and increases he total quantity present in solution. For Hagerstown loam the maximum absorptive capacity was found by extrapolation of the distribution curve to be approximately 1,700 parts per million. This means that with very great concentration of manure in solution 1 kilo of this soil would absorb 1.7 grams of soluble manure from the extract and no more. The data does not admit of calculating the maximum absorptive capacity for the other two soils, but a comparison of the soils on the basis of the highest quantity of manure absorbed by each gives a ratio of 2.7:2:1, in the order: Hagerstown loam, Marshall silt loam, and Norfolk sand. Here the order of the absorptive capacity is the reverse of that found for gentian violet as shown in Table IV, where Marshall silt loam had nearly twice the absorptive power found for the Hagerstown loam.

RELATION OF DISTRIBUTION TO THE USE OF FERTILIZERS.

This series of experiments is important in showing that absorption is dependent as much on the nature of the solute as on that of the absorbent. It further indicates the probable futility of attempting to select empirically a dye with which quantitative measurements might be made to determine the absorptive power of a soil for manures or fertilizers, or to determine its relative crop-producing power.

The experiments with gentian violet, together with those using manure, in Tables IV and VI, show that when fertilizers are applied to a soil relatively less and less soluble matter is absorbed from the fertilizer as more and more fertilizer is added to the same area. But on any given tract the *percentage* of fertilizer absorbed is greatest where the least fertilizer is used.

The usual application of fertilizers, however, does not raise the concentration of the soil solution appreciably. This is due to the fact that soils in the field can still absorb far more of the fertilizer constituents, and the conditions are represented by the steep portion of a distribution curve, in which region the soil absorbs large quantities of soluble material, leaving the solution very little different from the original soil solution.

Several of the cases given above for the distribution of a solute between water and soil can be represented by straight lines, that is, they can be described by a linear function of the form $C/C_1=K$. In what appears to be the more general type of distribution, however, the data do not accord well with the equation $C^n/C_1=K$, but with equations of a more complex form; in fact, for some distribution curves, when the logarithms of C and C_1 are taken and plotted, a curved line results, showing that *no exponential equation* describes this particular distribution curve. As these complex equations have no special significance and are purely empirical, they are not given here. One reason for these deviations from the simpler forms of the distribution equation was apparent in the marked changes in the state of aggregation or "flocculation"[a] of the soil particles induced by different concentrations of the solute in the aqueous solutions. In the absorption of eosine by quartz, where the distribution was nearly linear, there was no flocculation of the absorbing grains which could be observed; but the same quartz flour was flocculated when absorbing gentian violet, and very differently at different concentrations of dye. Moreover, the extent of the flocculation with increasing amount of dye went through a maximum, so that no simple formula could be expected to hold for the distribution curve. The soils studied showed similar flocculation phenomena. The foregoing data and considerations lead to the following conclusions:

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[a] Patten, Trans. Am. Electrochem. Soc. **10**, 67 (1906.)

(1) The distribution of solute between solvent and absorbent presents in general the same characteristics with soils as with other absorbents.

(2) For any series of soils or other absorbents the order of the absorptive capacities for one solute may be entirely different from the order for another solute.

(3) With one and the same soil or other absorbent the distribution function may be linear for one solute and asymptotic for another.

(4) Generally when soils are the absorbents the change of surface or "flocculation" introduces a modifying factor and the form of the distribution equation is rendered more complex.

EFFECT OF TEMPERATURE UPON DISTRIBUTION.

Biedermann[a] studied the effect of temperature upon absorption from solution. His results are not concordant, but are nevertheless what might have been expected when the effect of temperature upon humus and upon the various soil constituents, such as calcium carbonate, are considered. In general, for phosphates, the higher the temperature, up to 100° C., the greater the absorption, and after boiling for fifteen minutes still more solute was fixed by the soil. There are exceptions to this rule, where the absorption is less at higher temperatures; for potassium the absorption decreased with rise in temperature for five out of nine soils.

Bayliss[b] has further shown that the rate at which Congo-red is taken up by paper is accelerated by rise of temperature, but the total amount taken up when equilibrium is reached is less the higher the temperature; the temperature coefficient of the reaction velocity is very low, so that Nernst's theory as to the part taken by diffusion in heterogeneous reactions seems to apply to adsorption. At low temperatures, equilibrium is attained slowly; at room temperature, twenty-four hours is necessary. The adsorption complex of gelatine and inorganic electrolytes is also dissociated as the temperature rises, and no evidence of heat production in adsorption is obtained. The reaction between Congo-red and paper is reversible; so also is that between gelatine and electrolytes. It is, however, noticed that raising the temperature rapidly to 100° C. tends to fix Congo-red in paper.

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[a] Landw. Vers.-Stat., **11**, 1 (1869).

[b] Biochem. Jour., **1**, 175 (1906).

Draper and Wilson [a] have shown [b] that "bleu de nuit" may be absorbed by silk in two different manners, depending upon the temperature at which the dyeing takes place. Above 40° the dyed fabrics are much more resistant; at 15° the dyed fabrics "fade out" by a treatment with "soap solution" or with alcohol. When the temperature of the bath is raised, a part of the dye is fixed more firmly. These experiments have been extended to acid dyes. The silk dyed with anthracene red, acid 3B, employing 0.25 per cent of the dye in a solution of acetic acid, 0.2 per cent, offered a resistance to "soap solution" greater according to the temperature. If one makes the treatment with a solution of 1 per cent of neutral soap solution heated to 55° C. and allows an immersion of thirty minutes, the following results are obtained:

TABLE VII.—*Effect of temperature upon absorption according to Draper and Wilson.*

Temperature of the bath.	Dye remaining upon the absorbent.	Temperature of the bath.	Dye remaining upon the absorbent.
°C.	*Per cent.*	*°C.*	*Per cent.*
18.5	0.002	75	0.13
40	.01	90	.18
60	.11		

RATE OF ABSORPTION.

FORMULA EXPRESSING RATE OF ABSORPTION.

The simplest assumption that can be made is that the rate of absorption is proportional to the quantity of solute which the absorbent may yet take up; that is, to the difference between the specific absorptive capacity as defined on page 43 in this bulletin and the amount of solute already taken up. If in time t, the absorbent has taken up the amount of solute, y, while its specific absorptive capacity for a solution of that particular concentration is A, then the above assumption can be formulated thus:

$$\frac{dy}{dt} = K(A-y)$$

where K is the constant of proportionality for the particular absorbent and solution under standard conditions. In the following paragraphs a few typical cases will be described for various absorbents, including soils.

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[a] Jour. Soc. Chem. ind., **26**, 667 (1907).

[b] Jour. Soc. Dyers and Colorists, **22**, No. 9.

In testing this rate equation with the observed data, it will be more convenient to use the integrated form, namely,

$$\log (A-y) - Kt = \log A$$

which is a linear function with respect to $\log (A-y)$ and t. Since no special significance attaches to the constant K, Briggsian logarithms may be used for convenience. From inspection of this integrated equation it is evident that when the values $\log (A-y)$ are plotted against t a straight line results if the original differential equation, $\frac{dy}{dt} = K(A-y)$, correctly describes the rate of absorption.

EXPERIMENTAL TESTS OF FORMULA.

RATE OF ABSORPTION OF POTASSIUM BY A SOIL.

Peters[a] has determined the rate at which a soil absorbs potassium from an aqueous solution of potassium chloride. He does not give the temperature, but states that the experiments were carried out at Tharand in the summer of 1860 at room temperature. His results are given in Table VIII, where t represents the time in hours; y, the grams potassium oxide absorbed by 100 grams of soil; and $\log (A-y)$, the value calculated from A, 0.2168—the specific absorptive capacity of the soil for the end concentration of solution—less the value of y at each time given in the table under t.

When $\log (A-y)$ is plotted against t, the graph is not a straight line; and, in addition, $\log A$ as estimated by extrapolating the curve is less than the value of $\log A$ as found by experiment. Consequently it follows that the formula $\frac{dy}{dt} = K(A-y)$ does not describe the actual rate of absorption observed by Peters.

TABLE VIII.—*Rate of absorption of potassium oxide by a soil, according to C. Peters.*

[100 grams soil and 250 c. c. of 0.05 N potassium chloride solution.]

Time.	K_2O absorbed $= y$.	$\mathrm{Log}(A-y)$.	Time.	K_2O absorbed $= y$.	$\mathrm{Log}(A-y)$.
Hours.	*Gram.*		*Hours.*	*Gram.*	
0.25	0.1417	$\bar{2}.814$	8	0.1860	$\bar{2}.499$
2	.1571	$\bar{2}.776$	24	.1990	$\bar{2}.251$
4	.1690	$\bar{2}.679$	48	.2168	....

RATE OF ABSORPTION OF OXALIC ACID BY ANIMAL CHARCOAL.

Lagergren[b] has determined the rate at which animal charcoal absorbs oxalic acid, and, using the reaction velocity equation of the first order $\frac{dy}{dt} = K(A-y)$, he has calculated a series of values of y, which are given together with those for t and y in Table IX. A is taken as the maximum quantity of oxalic acid absorbed. His calculated values do not agree with the experimental values of y sufficiently well to warrant the use of this equation.

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[a] Landw. Vers.-Stat., **2**, 127 (1860).

[b] Bihang K. Sv. Vet. Akad. Handl., Band 24, Afd. II, No. 4, ii (1899).

TABLE IX.—*Rate of absorption of oxalic acid by charcoal, according to Lagergren.*

[Five grams charcoal and 10 c. c. of solution containing 4.241 grams oxalic acid per liter.]

Time, t.	y—oxalic acid absorbed.	Calculated value of y.	Time, t.	y—oxalic acid absorbed.	Calculated value of y.
Minutes.	*Gram.*	*Gram.*	*Minutes.*	*Gram.*	*Gram.*
5	0.046	0.042	180	0.245	....
10	.090	.076	360	.227	....
30	.151	.163	2,880	.249	....
60	.198	.215			

RATE OF ABSORPTION FROM PERCOLATING SOLUTIONS.

Schreiner and Failyer[a] have studied the rate at which phosphates and potassium are absorbed from solution passing through typical soils. A solution of definite concentration was percolated through soils, maintaining the rate of percolation constant by an automatic device, and determinations were made of the concentrations of solute, which increased in the successive percolates. It was found that each soil had its own specific absorbing power and that the process of absorption, considered as a volume rate, gave very regular curves when the quantity of phosphate absorbed was plotted against the total volume of solution which had been percolated. It was shown that the volume rate of absorption was well described by the differential equation

$$\frac{dy}{dv} = K(A-y)$$

where A is the "specific absorptive capacity" of the soil for phosphates in equilibrium with the solution, y is the quantity of phosphate which the soil has taken up from solution after v c. c. of that solution has passed through the soil, and K is a constant—the velocity constant. As the liquid passes from top to bottom each layer exerts its absorbing power upon weaker and weaker solution, and consequently the rate equation

$$\frac{dy}{dv} = K(A-y)$$

is a summation of all these various rates of absorption.

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[a] Bul. No. 32, Bureau of Soils, U. S. Dept. Agr. 1906; Jour. Phys. Chem., **10**, 239, 361 (1906). Compare, Calugareanu and Henry, Compt. rend. Soc. Biol., **53**, 579 (1901). Diffusion of dye stuffs through gelatine.

RATE OF PERCOLATION THROUGH SOILS.

Seelheim[a] has examined quantitatively the factors which determine the rate of percolation through sand, clay, and calcium carbonate, and finds that Poiseuille's formula, $Q = C/L$, holds for all three solids. A mixture of two sands, one having grains small enough to lodge in the interstices between the grains of the other, gives very nearly (about 1.2 times greater) the percolation rate of the smaller grained sand. But where the two sands have grains more nearly of the same size, the percolation rate is the average of that for each sand separately. The rate of flow is directly proportional to the head of water and inversely to the thickness of the soil layer. Where several layers of soil are superposed, the speed of percolation is essentially that of the least permeable layer. The acceleration in flow due to increase in temperature was determined, and an interpolation formula, calculated by means of least squares, is given for the sand, clay, and chalk used.

RATE OF MOVEMENT OF LIQUIDS THROUGH CAPILLARY TUBES, AND THROUGH PAPER AND POROUS MEDIA.

The work of Cameron and Bell[b] on the rate of movement of liquids through capillary tubes and through paper and porous media gives a slightly different treatment of the rate of absorption during percolation. In their first paper an empirical equation was proposed to describe the movement of water and of aqueous solutions through blotting paper and through soils:

$$y^n = Kt$$

where y represents the distance through which the liquid has moved in the time, t, and n and K are constants depending upon the temperature and the specific substances. The second paper places this empirical equation upon a rational basis by deriving it from the formula of Poiseuille[c] for the movement of a liquid from one level to another through a capillary tube: $Q = C\dfrac{HD^4}{L}$ where Q is the quantity of liquid passed through in unit time; H is the difference in level, or "head;" D and L are the diameter and length of the tube, respectively; and C is a constant. This equation may be applied to the advance or retreat of water in a capillary tube only when the assumption is made that the energy gained or lost with change of velocity (the "velocity head") is negligible in comparison with the energy gained or lost in the change of level of the water or in the friction against the walls of the tube. This formula was found to hold very well for the movement of several pure solvents through capillary tubes.

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[a] Zeit. anal. Chem., **19**, 387 (1880).

[b] Bul. No. 30, p. 46, Bureau of Soils, U. S. Dept. of Agr. 1905; Jour. Phys. Chem., **10**, 658 (1906).

Ann. Chim. Phys. (3), **7**, 50 (1843).

Several series of experiments were made by Bell and Cameron using blotting paper and soils with water, aqueous potassium chloride solution, and aqueous sodium eosine, indigo-carmine, and coralline solutions, and the formula was found to hold in every case, with the restrictions that the acceleration be negligible in comparison with the velocity and that the length of the capillary soil tubes be great in comparison with their diameters. And, in addition, they have shown that this equation describes the movement through soils and paper of solutions which suffer change during the process. Both the advance of the solute and of water in the medium conform to this formula.

RELATION OF DISTRIBUTION TO RATE OF ABSORPTION FROM A PERCOLATING SOLUTION.

These rate-of-advance studies of Cameron and Bell are related to the percolation studies of Schreiner and Failyer. The latter maintained the rate of flow constant and plotted the total quantity of solute absorbed against the volume of solution percolated. It will require a long period of time to bring the lower layers of soil to anything like saturation with respect to the solute in question, so that throughout the percolation experiment there will be a different concentration of solution in contact with each layer of soil from top to bottom of the percolation tube.

The rate of selective advance in soils for indigo carmine and water through the Penn loam, for coralline and water through the Penn loam, and for coralline and water through the Podunk fine sandy loam shows that the advance of the dye is slower than that of the water, and is different for each dye. This means, of course, that the absorption effect exerted by the soil upon the solution robs it of nearly all the dye, until a point on the distribution curve is reached where the solution can retain sufficient dye to carry it along by percolation to the next layer of absorbent. Thus we are not in reality studying the rate of flow of the dye or of the dye solution in these experiments, but rather the retaining ability of the various absorbent materials for the dye as its solution percolates. When the absorbent material is fairly well saturated with the dye, the rate of flow will differ,[a] but not greatly, from that of water, save as the addition of distilled water changes the distribution and thus induces a flocculation or deflocculation of the grains of the absorbent, thus altering the channels in the soil and the diameters of the capillary soil tubes.

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[a] Krakow, Jour. Landw., 48, 209 (1900), on comparing pure water and solutions side by side, found that the water moved more rapidly through a soil. Briggs and Lapham, Bul. No. 19, Bureau of Soils, U. S. Dept. Agr. 1902, p. 6, made the same observation, which they attribute to the greater viscosity of the solutions.

The absorption curves of Schreiner and Failyer are necessarily asymptotic, since the soil can absorb only a limited weight of salt from any given solution. Consequently their curves might be expected to fit some equation in which the dependent variable tends to a limiting value. This was found to be the case, the formula $\frac{dy}{dv} = K(A-y)$ serving remarkably well to describe their experimental results and others obtained in this laboratory.

The same consideration applies to the rate studies of absorption in general, viz, that there is a limit to the quantity which an absorbent can take up and retain under equilibrium conditions; therefore all curves plotted with quantity of substance absorbed as ordinate, y, and time of absorption, t, as abscissa, must necessarily tend to an upper limit for y. Consequently no exponential equation of the form $y^n = Kt$ can exactly describe absorption rate curves. For, when the time is infinite, the absorption, y, likewise is infinite; and this is contrary to experience.

Similarly in the rate-of-advance studies: The formula $y^n = Kt$ postulates that when $t = \infty$ the height of the liquid in the soil shall be infinite. This, again, is contrary to experience, the capillary water rising until its weight balances that of the capillary effect. But the formula was developed correctly enough for the advance or retreat of liquid in a horizontal capillary tube where y for all practical purposes is infinite, and the driving force, the capillary column of liquid, remains constant. With blotting paper, too, the formula was found to hold for short distances whether the paper was in a horizontal position with $y = \infty$; or held vertically with y approaching a limit. The application of this formula, then, to vertical columns of soil and blotting paper is justifiable, in that it enables us to handle and compare and analyze experimental data in a more satisfactory manner than by merely plotting the curves. But it should be borne in mind that the formula $y^n = Kt$ can not rigidly express any function which tends to a limiting value. This caution is emphasized here, since a number of rate curves are described by this formula for a limited range.

ENERGY CHANGES.

In general the treatment of energy change takes the form of measuring the change produced in properties of one substance by action upon it of a second. The energy in a body that is available for producing changes in another substance, or substances, other than heat is called the free energy. It is different at different temperatures, since the heat-capacity or energy-capacity of a body changes with the temperature.

When a body adsorbs another, one may expect several different energy changes, mainly—

(1) In cohesion and in surface energy.

(2) In work done on expansion or contraction of volume.

(3) Electrical effects; such as static charges on surfaces and upon suspended particles, and change in potential difference where metals are immersed in electrolytes.

(4) Heat effects; heat evolved or absorbed due to change in heat capacity, and due to a rearrangement of the whole system.

TEMPERATURE RISE CAUSED BY MOISTENING POWDERS.

Pouillet[a] observed a rise in temperature when various powders were moistened by different liquids using for this purpose—water, oil, alcohol, and ethyl acetate. As absorbents he used finely divided metals, metallic oxides, powdered glass, clay, and a number of organic substances.

A number of investigators have measured the rise in temperature occasioned by the absorption of various vapors by dry soils and other absorbents. A discussion with citations of this literature has recently been given,[b] and need not be repeated here.

CHANGE IN DENSITY OF ABSORBED LIQUIDS.

Hassenfratz[c] claimed that a substance such as glass after being powdered showed a smaller specific gravity than before, and that the adherence of air to the powder does not account for the phenomenon. But he gives one experiment *using the same sample of glass powder* in which the density obtained on weighing the glass under water in an evacuated flask was greater for the powdered glass than for the same glass in one sheet. Since this agrees with the results of later investigators, it is very likely that the other observations of Hassenfratz—where he found a lower density for the glass in powder form—were affected by incomplete removal of the absorbed gases from the glass. He has, however, shown very well by these experiments that a powder placed in a liquid and thoroughly stirred will retain a considerable quantity of gas, and that the last traces of this absorbed gas are very difficult to remove, even when the liquid containing the powder is placed in a vacuum.

In the case of water wetting a powder, Junk[d] found that above 4° C. there was an increase in temperature, and below 4° C. a decrease in temperature. This result is attributed to an increase in density at the surface of the powder, which above 4° C. would tend to increase the temperature of the mass of the liquid, and below 4° C. would decrease the temperature. Meissner,[a] however, has more recently found an increase in temperature at 0° C.

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[a] Ann. Chim. Phys., **20**, 141 (1822); Gilbert's Ann., **73**, 356 (1823).

[b] Bul. No. 51, Bureau of Soils, U. S. Dept. Agr.; Trans. Am. Electrochem. Soc. **11**, 387, 1907.

[c] Gilbert's Ann. **1**, 396 (1799).

[d] Pogg. Ann., **125**, 292 (1865).

ESTIMATION OF THE PRESSURE IN ADSORBED LIQUIDS.

Lagergren[b] has calculated the pressure of water at the surface of a solid consequent upon the increase in density, and finds a pressure upward of 6,000 atmospheres. Young[c] estimated its value for water at 23,000 atmospheres, while Lord Rayleigh[d] mentions with approval a hypothesis of Dupré, which leads to the value 25,000 atmospheres by a deduction from the dynamical equivalent of the latent heat of evaporation of water. A change in density has also been noted by Spring,[e] who found that the amount of water required to fill the spaces of a given mass of sand was greater than would be expected if it were merely a phenomenon of occupying the air spaces. This phenomenon has been ascribed to an increase in the density of the water at the surface.

TEMPERATURE INCREASE CAUSED BY MOISTENING SOILS.

Stellwaag[f] found the following increases in temperature by moistening soils and soil constituents with water: 8.33° C. for a calcium carbonate sand rich in humus; 6.6° C. for ferric hydroxide; 5.57° C. for a loam soil.

HEAT EVOLVED ON WETTING QUARTZ POWDER.

Martini[g] gives 13.73 calories as the heat evolved on wetting 1 gram of quartz powder with water. A mechanical analysis of the powder is not given. Similarly, charcoal evolved 14.45 calories per gram when placed in water. Ercolini[h] finds slightly different values: 13.23 calories for quartz, and 14.23 calories for charcoal.

HEAT EVOLVED ON WETTING CHARCOAL WITH VARIOUS LIQUIDS.

Martini[i] found each liquid has its own heat of wetting. Thus with granulated animal charcoal at 17°–18° C. water showed a rise in temperature of 15.58°; absolute ethyl alcohol, 17.47°; ethyl ether.

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[a] Wied. Ann., **29**, 114 (1886).

[b] Bihang. till K. sv. Vet.-Akad., Handl. 24, Afd. II, No. 5 (1898).

[c] Minchin, Hydrostatics and Elementary Hydrokinetics, 311 (1892).

[d] Phil. Mag., (5) **30**, 473 (1890).

[e] Mem. Soc. Geol. Belge, **17**, 13 (1903).

[f] Forsch. Geb. Agr. Phys., **5**, 211 (1882).

[g] Atti del R. Istituto Veneto (7) **9**, 958 (1897).

[h] Nuovo Cimento (4) **9**, 110 (1899).

[i] Atti del R. Istituto Veneto (7) **8**, 510 (1896).

17.50°; ethyl acetate, 18.94°; benzene, 17.60°; carbon disulphide, 20.60°. It is interesting to note, too, that benzene with impure charcoal gave no rise in temperature, and that amyl alcohol showed this same indifferent action, evolving no heat. Absolute alcohol caused a rise of 5.55° only, whereas less pure alcohol showed 10.03° rise. Unfortunately, data are not available for the conversion of these observations to calories.

Linebarger,[a] using the same sample of quartz powder with which Martini worked, found 13.80 calories evolved per gram when placed in water; 11.21 and 10.88 calories for nitrobenzene; 9.61 and 7.55 calories for toluene; 4.09 calories for benzene; 11.84 and 12.46 calories for pyridine. The granules of this powder had an average diameter of 0.0005 cm. Using another sample, with average diameter of grain, 0.00096, Linebarger found that practically half the quantity of heat given above for each liquid was evolved on wetting. He found, in common with previous investigators, that the relative quantity of liquid does not influence the heat effect. A certain minimum quantity of liquid is necessary to produce the maximum heat change, but any excess of that amount has no perceptible influence. The heat effect per unit mass of the powder is the same for the same liquid at the same temperature, provided this minimum amount be present.

HEAT EVOLVED BY POWDERS ON ABSORBING WATER VAPOR.

The experiments of Parks[b] indicate that the heat which water vapor liberates when it condenses upon the surface of the silica grains is returned to the liquid water (which is in the vessel with the silica to maintain the air space saturated with water vapor) as it evaporates to take the place of the water vapor which the silica had adsorbed. In the end, therefore, the same quantity of water is adsorbed and the same quantity of heat liberated when the silica is in contact with water vapor as when it is placed under liquid water.

PARKS'S LAW.

In another paper[c] Parks formulates a law, "When silica, sand, or glass is brought in contact with water, at approximately constant temperature, the heat evolved is proportional to the area of the surface exposed by the solid, and the amount of heat developed per square centimeter is approximately 0.00105 calorie when the temperature is near 7° C." And for a range of 17°, from 7° C. to 24.3° C., this heat evolution increases 0.0000035 calorie per square centimeter of surface for each degree increase in temperature. It has been suggested that this law of Parks's may be used to ascertain the area of a powder or a soil per gram by determining experimentally the heat evolved when the powder is placed in water and dividing this quantity of heat by the calories which 1 square centimeter of surface liberates when wetted. But here again we meet the same difficulty which confronted Kayser[a] in his attempt to determine the area of the surface presented by the grains of powder by measuring the quantity of water adsorbed by the powder and then dividing this weight of water by the number of grams of water adsorbed upon a surface of standard material. He failed to find a standard material. Each surface tried showed a different degree of adsorption. The researches quoted above show that each soil constitutent has its own heat effect when moistened; consequently, an attempt to measure the area of a soil in this manner is not promising.

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[a] Phys. Rev., **13**, 48 (1901).

[b] Phil. Mag. (6), **5**, 521 (1903).

[c] Phil. Mag. (6), **4**, 247 (1902).

In Linebarger's experiments[b] the heat evolved compared to the surface of silica exposed is greater than that shown by Parks. But in considering this apparent clash of results one must bear in mind that Linebarger has measured the heat effect of the same solid in different liquids and finds the ratio of the different heat effects for coarse and fine powder the same in different solvents. This is very strong evidence, indeed, that the heat evolved is proportional to the surface. The error involved in calculating the effective area of a powder is enormous. Parks's values involve the area as calculated from microscopic measurement of the granules. Linebarger's ratio is absolute, since he takes merely average samples of each grade of powder, without attempting to evaluate the area, and uses these two samples with each liquid.

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[a] Wied. Ann., **24**, 450 (1885).

[b] Phys. Rev., **13**, 48 (1901); see also:
Cantoni, Rend. del R. Istituto Lombardo, Class di Scienze Matematiche e Naturali, **3**, 135 (1866);
Martini, Atti del R. Istituto Veneto, (7) **8**, 502 (1896); (7) **9**, 727 (1897); (8) **2**, 615 (1900);
Tait, Proc. Roy. Soc. Edinb., **11**, 51 (1880–81); **11**, 813 (1881–82);
Marshall Smith and Omond, Ibid. **11**, 626 (1881–82);
Amagat, Compt. rend., **116**, 946 (1893);
Lussana, Nuovo Cimento (4) ii, 233 (1895);
Lagergren, Köngl. Vet. Akad. B. **24**, Afd. ii, Stockholm, (1899);
Tate, Phil. Mag. (4) **20**, 508 (1860);
Melsens, Mem. Acad. Belg., **23**, (1873); Ann. Chim. Phys. (5), **3**, 522 (1874);
Chappuis, Wied. Ann., **19**, 21 (1883);
Wiedemann and Lüdeking, Wied. Ann., **25**, 145 (1885);
Gore, Phil. Mag., **37**, 306 (1894); Birm. Phil. Soc. Proc., **9**, part 1, (1893).
Ercolini, Nuovo Cimento (4) **9**, 110 (1899);
Bellati, Atti del R. Istituto Veneto (8) **2**, 931 (1900);
Fitzgerald, Nature, **49**, 293, 316 (1894);
Weber, Pogg. Ann. 154, 367 (1875);
Barus, Phil. Mag. (6), **4**, 24, 262 (1902);
Magnus, Phil. Mag. (4), **6**, 336 (1853).

HEAT EVOLVED BY SWELLING STARCH.

Rodewald[a] has studied quantitatively the energy changes of starch as it absorbs water. One specimen evolved 24.02 calories per gram of starch; another, 19.4 calories. He finds that the greatest available effect in the passage of heat into work which can be reached in the swelling of starch is 11.4 per cent of the total heat effect, which latter is 24.02 calories. This result is based upon measurements of volume change during swelling. The average pressure between the ultramicroscopic cells of starch is calculated as 2,137 atmospheres, while very near to a cell wall the pressure would be much greater. Comparing this value with those of Dupré (25,000 atmospheres) and Young (23,000 atmospheres) and Lagergren (6,000 atmospheres), it seems probable that in the swelling of starch the imbibition effect predominates over the absorption.

COMPENSATING FACTORS THAT MASK THE ENERGY CHANGE IN ABSORPTION OF MATERIAL FROM SOLUTION.

The foregoing citations contain only the heat changes consequent upon the wetting of powders and the absorption of vapors. No values for the energy change accompanying absorption from solution are available, although it is possible to make such measurements. This phenomenon is analogous to the general problem of the energy changes attendant upon the process of solution. In this case the determinations of the individual forces at work is difficult; the actual heat and volume changes measured are the resultant of all the forces involved. Among these are the attraction of solvent and solute and the cohesion of the solute. Some idea of the cohesion of the solute may be obtained from its heat of vaporization. In like manner it is difficult to estimate the individual forces in the case of absorption from solutions, for there are the added factors of the attractions of the absorbent for both solvent and solute. At present the best indication of the magnitude of these forces is the chemical decomposition which they produce—decompositions which, effected in other ways, require large quantities of energy.

THE CONDITION OF THE ABSORBED SUBSTANCE.

THEORIES PROPOSED.

The earlier theories of absorption, and more especially of adsorption, were based either upon the assumption of a pressure at a surface layer of liquid higher than that in the free liquid or upon the theory of wetting of a solid by a liquid.

Only at the saturation point is it possible to consider the effect of pressure upon the solubility. The case of absorption from unsaturated solution must be considered as a distribution of the solute between layers of the liquid at different densities. This is analogous to the distribution of a solute between two different liquids or to the Soret effect, obtained when different portions of the solution are maintained at different temperatures, resulting in two solutions of different concentrations. The effect of pressures has been discussed by various authors.[a]

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[a] "Researches on the Swelling of Starch," Lipsius and Fischer, Leipsig, 1896.

From the principle of Le Chatelier [b] it follows that if on solution contraction occurs there will be a positive adsorption, i. e., the surface layers will become more concentrated.

A theory of absorption from solution has been based upon considerations of the surface tension between solid and liquid,[c] which tension there is no direct method of determining experimentally. It has, however, been derived from the theory of wetting of a solid by a liquid, and is shown to be less than the surface tension between solid and gas. In case the surface tension between solid and liquid is lowered by the addition of a substance soluble in the liquid, it follows that there will be adsorption of the substance on the surface of the solid, for the potential surface energy will tend to become lower by further concentration at the bounding surface.

PHYSICAL ABSORPTION.

Without entering deeply into the distinction between chemical and physical change, we may for practical purposes define a physical change as one in which the altered substance retains sufficient of its former characteristics to be recognizable as the same material present before the change took place.

On the basis of this definition we may classify a number of absorption reactions as physical changes, in that the dissolved substance as a whole is concentrated in the layer of liquid close to the absorbing solid, and in some cases even deposited upon its surface in a condition nearly or quite solid.[d] A good example of this is the adsorption of the organic dye gentian violet (gentianin) by quartz powder. Here the dye is retained in a thick layer upon the grains of quartz while the solution bathing the quartz is a thousand to ten thousand parts per million below its saturation point for this dye. Under the microscope the dye upon the quartz grains shows its characteristic colors for reflected and transmitted light, and when the dyed powder is subjected to percolation with distilled water the dye is gradually removed and recovered intact.[a]

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[a] Thomson, Applications of Dynamics to Physics and Chemistry, p. 237–240; Freundlich, Zeit. phys. Chem., **57**, 422 (1906); see also Lagergren, Bihang t. k. Sv. Vet. Akad. Handl., **24**, 2, No. 4 and 5 (1899); Parks, Phil. Mag (6) **4**, 240 (1902); (6) **5**, 517 (1903).

[b] See Bancroft, Phase Rule, p. 4 (1897).

[c] For references, see Freundlich, Zeit. phys. Chem., **57**, 421 (1906).

[d] Thomson, Applications of Dynamics to Physics and Chemistry, 1888, p. 91; Freundlich, Zeit. phys. Chem., **57**, 385 (1906); Ostwald, Lehrbuch der Allgemeine Chemie, (1891), p. 1096; Frank K. Cameron and James M. Bell, Bul. No. 30, Bureau of Soils, U. S. Dept. Agr. 1905.

In some cases the adsorbed material is retained in solution in the layer of liquid close to the surface of the solid. This is very well shown for alkaline carbonate solution with soil. The fine clay particles when suspended in the solution produce no appreciable lowering of the electrical conductivity, but when they are removed by centrifiugal action or by settling the quantity of adsorbed material which they carry down with them is sufficient to reduce the conductivity of the supernatant liquid to a marked degree.[b] And since these carbonates, or any chemical compounds they might form, have a low conductivity as solids it follows that they are present in solution at the surface of the soil particles and contribute to the conductivity of the main body of liquid in which the soil is suspended. Should the clay contain hydrated silica, alumina, or ferric oxide in an amorphous condition, part of the solution will be imbibed by them and removed when the suspension is cleared by settling; but in this case, too, the fact that the absorbed material contributes to the electrical conductivity shows that it is still in solution.

ABSORPTION BY CHEMICAL FIXATION.

In addition to these three types of physical absorption, we may have chemical fixation of dissolved bodies at the surface of a solid. The solute may be removed from solution as a whole and added to the solid absorbent to form a compound. Thus metallic silver will absorb chlorine from solution forming silver chloride. The absorbing solid, too, may lose some constituent at the same time that it absorbs the solute. Solid calcium hydroxide absorbs carbon dioxide from solution and loses water. Much more complicated replacement reactions between soil constituents and soil solution take place, as set forth at length in a previous bulletin.[c]

Since many cases of absorption are known in which both physical and chemical changes occur, the above classification, although convenient, should not be rigidly applied. Indeed, all gradations of union are possible, from purely physical surface adhesion—which still depends upon the composition of the bodies involved—to purely chemical combinations. One important intermediate step may be solution, either liquid or solid.

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[a] Trans. Am. Electrochem. Soc., **10,** 67 (1906).

[b] Electrochem. and Met. Ind. **5,** 257 (1907).

[c] Bul. No. 30, Bureau of Soils, U. S. Dept. Agr., 1905.

CALCULATION OF THE PROBABLE THICKNESS OF ADSORBED MATERIAL.

A series of calculations for several soils is presented in Table X. The concentration of gentian violet dye solution at the surface of soil grains is estimated from the quantity of hygroscopic water and from the quantity of dye absorbed by the soil. This involves the assumption that the hygroscopic water determined by allowing dried soil (110° C.) to take up moisture from a saturated atmosphere is the same in quantity as the moisture retained upon the soil grains when the soil is in a saturated condition.[a] The results not only show the magnitude of the surface concentration, but also are of value in studying the physical condition of soils.

TABLE X.—*Relation of gentian violet dye absorbed to area of soil and to hygroscopic water.*

Soil.	Dye absorbed per 100 grams soil.	Hygroscopic water per 100 grams soil.	Dye in solution on soil grains.	Volume of solution retained by 100 grams of soil.	Area of soil per gram.
	Grams.	*Grams.*	*Per cent.*	*C. c.*	*Sq. cm.*
Marshall silt loam	0.3	4.0	7.0		2,320
	.485	4.0	10.8	47	
	.9999	4.0	20.0	50	
	1.50	4.0	27.3	47	
	1.999	4.0	33.3		
	2.497	4.0	38.4		
	2.991	4.0	42.8		
	3.119	4.0	43.8		
	3.70	4.0	48.1		
Hagerstown loam	.0	4.5		61	
	.20	4.5	4.3	56	2,270
	.4	4.5	8.2	54	
	.5	4.5	10.0	55	
	.998	4.5	18.1	57	
	1.495	4.5	25.0	50	
	1.981	4.5	30.6	45	
	2.045	4.5	31.3		
	2.025	4.5	31.0		
Quartz flour	.000	.8		36.5	1,200
	.019	.8	2.32	36	
	.038	.8	4.53	38	
	.075	.8	8.58	48	
	.098	.8	10.90	50	
	.190	.8	19.20	46	
	.265	.8	25.0	40	
	.289	.8	26.52	37	
	.295	.8	26.93	34	
	.297	.8	27.03	30	
	.293	.8	26.80	29	

Gentian violet is not very soluble in water, a 2 per cent solution being viscous and 6.81 per cent its solubility at 25° C.; yet the calculated per cent of dye in solution on the soil grains is 48.1 for Marshall silt loam, 31 for Hagerstown loam, and 27 for quartz flour. Although the hygroscopic moisture held by the quartz is less than one-fifth of that of the Hagerstown loam, the percentages are in very close agreement. The percentage of dye held in solution is actually higher than these values given, since the dye absorbed is in or on the soil grains, while part of the hygroscopic water should be reckoned as capillary water and is the same in concentration as the supernatant solution from which the dyed soil grains have settled out.

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[a] Parks, Phil. Mag. (6), 5, 521 (1903).

Since the calculation just made gives such high values for the concentration of dye upon the soil grains, it may even be that the dye is not in solution in the surface layer, but has separated upon the grains as a solid. The work of Rohde[a] is in line with this. He states that the aqueous solutions of fuchsine and methyl violet form at their surfaces solid layers which through their metallic luster are unmistakably evident to the eye. The surface of the liquid becomes first more concentrated, then viscous, and finally stiff and solid, so that in the condition of equilibrium the solution is covered with a skin of solid dyestuff.[b]

Rohde says, again, that the solid surface layer is the thicker and forms the faster the more concentrated the solution. According to his calculations the thickness of the layer (of solid dye) is always of a lower order of magnitude than the radius of the sphere of action. The present calculation, however, shows that the layer of dye on the grains of quartz flour, Marshall silt loam, and Hagerstown loam is many fold that of the calculated molecular dimensions. This is also true for the absorbed layer of eosin and for manure extract, and aside from these calculations microscopic examination shows a very appreciable layer of dye on the grains.

EFFECT OF ABSORPTION UPON THE PHYSICAL CONDITION OF THE SOIL.

RELATION OF ABSORPTION TO THE FORMATION OF AGGREGATES.

The absorption of nutrient salts by the soil not only maintains a proper soil solution, but also exercises a marked influence upon the size of the soil aggregates. This soil structure in turn governs the water-holding power, the porosity, and consequently the aeration of the soil; and these factors are of the utmost importance to the bacterial life in the soil, as well as to the changes in the organic and mineral constituents. The effect of absorption upon the soil solution has been discussed in several preceding chapters.

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[a] Ann. Phys., **19**, 935 (1906); see also the references given in the preceding sections.

[b] "Es spricht nichts gegen die Annahme, dass die molekularen Kräfte, welche die Ausscheidung des festen Farbstoffs bewirken, dieselben sind, wie bei der Oberflächenspannung der Flüssigkeiten tätigen. Es Würden namlich die grossen zwischen zwei Wasser moleküln wirkenden Kräfte, welche auch die grosse Oberflächenspannung des Wassers zur Folge haben, es bewirken müssen, dass die an der Oberfläche der Farbstoffslösungen befindlichen Farbstoffmoleküle, mit frosserer Kraft in das innere der Lösung gezogen werden, als die dort befindlichen Farbstoffmoleküle, was die bobachtete Anreicherung der Oberfläche an Farbstoff zur unmittelbaren Folge ergibt."

The present chapter has to do with the changes in the physical structure of the soil attendant upon the addition of various soluble substances, such as fertilizers and correctives and salt water from inundations. When a salt is absorbed by a soil in suspension, there may occur either the formation of larger aggregates or else the breaking up of aggregates already present. Larger aggregates settle more readily and occupy a larger volume, while the smaller aggregates or single grains settle much more slowly and into a compact bed.

The direct relationship between the absorption of soluble material by percolates in suspension and their settling has been shown by Linder and Picton,[a] as well as by Whitney and Ober.[b] Colloids which settle from suspension in neutral solution carry down small quantities of metallic hydroxides.

Several hypotheses have been advanced to account for the formation and breaking up of aggregates.

Many of the agents which produce flocculation have been found to be more or less hydrolyzed in aqueous solution, and the flocculating power has been attributed to this hydrolysis. Freundlich[c], however, has found that the flocculating power of barium salts, which are scarcely hydrolyzed, is almost equivalent to that of beryllium salts and uranyl nitrate, both of which are strongly hydrolyzed, and as all of these salts have bivalent cations this can not be attributed satisfactorily to the difference in valence.

Another theory growing out of their work attributes the precipitation of suspended particles to the ions of the salt in solution. The mechanism of this precipitation is such as to constitute the neutralization of the charge of electricity upon the suspended particles by the ions carrying the opposite charge. On the basis of their experiment, in which they used electrolytes and nonelectrolytes, it has been claimed by Barus,[d] Bodländer,[e] Freundlich,[f] and Whitney and Ober[g] that the power to flocculate colloids is possessed exclusively by electrolytes.[h]

The flocculation of colloids by electrolytes has been investigated by Schulze,[i] Hardy,[j] and many others, and there has been a tendency to correlate the flocculating power of an ion with its valence. Schulze found that the power of salts of univalent, bivalent, and trivalent metals to flocculate colloids was in the proportion of 1 to 30 to 1,650. This in turn has been ascribed by Bredig[a] and Spring[b] to the hydrolysis of the salt, the degree of which increases very rapidly as the valence of the cation increases.

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[a] Jour. Chem. Soc., **67**, 63 (1895).

[b] Jour. Am. Chem. Soc., **23**, 842 (1901); Zeit. phys. Chem., **33**, 385 (1901).

[c] Zeit. phys. Chem., **44**, 129 (1903).

[d] Am. Jour. Sci., **37**, 122 (1889).

[e] Nach. K. Ges. Wiss., Göttingen, 1893, p. 267.

[f] Zeit. phys. Chem., **44**, 136 (1903).

[g] Jour. Am. Chem. Soc., **23**, 842 (1901); Zeit. phys. Chem., **33**, 385 (1901).

[h] Compare, Kahlenberg. Jour. Phys. Chem. **6**, 1 (1902); **10**, 593 (1906).

[i] Jour. prakt. Chem. **133**, 431 (1882); **135**, 320 (1883).

[j] Proc. Roy. Soc., **66**, 111 (1900); Zeit. phys. Chem., **33**, 385 (1901).

Colloid suspensions have been divided into two classes: Those which migrate toward the cathode under electrical stress and those which migrate toward the anode. The colloids which migrate toward the anode are said to be precipitated by anions, and vice versa. This migration of the colloids resembles the behavior of an electrolyte, and the theory has been advanced that colloids in solution are in reality large aggregations with small electrical charges,[c] which are counterbalanced by the presence of ions carrying the opposite charge. Thus there would be an equilibrium between the two, and a disturbance of the equilibrium by the addition of a salt to the solution tends to precipitate the colloid. Further, both classes of colloidal suspensions have the peculiarity that any one is precipitated from the solution when added to a suspension of one of the other classes, the precipitate being of course a mixture of the two.[d]

Hilgard[e] has shown that increase of temperature decreases flocculation; alcohol and ether decrease flocculation, as do also alkalies, while neutral salts, acid, and lime promote flocculation. Whitney[f] has also given considerable attention to flocculation, especially its effect upon the adaptation of special crops to soils. At his suggestion Bliss[g] made a study of the precipitation of suspensions and found that sodium chloride and hydrochloric acid induced flocculation, while potash and ammonia inhibited it, and also that the concentration of the solution is a determining factor. Bodländer[h] has given the concentration of typical acids, bases, and salts required to precipitate kaolin suspended in water. Sachsse and Becker[i] have determined the percentage of several salts precipitated from suspension by lime water.

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[a] Anorganische Fermente, 1901, p. 15.

[b] Bul. Acad. Roy. Belg., 1900, 483.

[c] Duclaux, (Compt. rend., **140**, 1544 (1905)) considers the granules of a colloidal solution as of such magnitude that they may be regarded as conductors of electricity.

[d] Linder and Picton, Jour. Chem. Soc., **67**, 63 (1895); Freundlich, Zeit. phys. Chem., **44**, 129 (1903); des Bancels, Compt. rend., **140**, 1647 (1905).

[e] Forsch. Geb. Agr. Phys., **2**, 441 (1879); also Silliman's Jour., **17**, March, 1879; ibid, **6**, Oct. and Nov., 1873: See also S. W. Johnson, Rept. Conn. State Board Agr., 1877–1878, Hartford, 1878, The reasons for Tillage.

[f] Bul. No. 5, Division of Agricultural soils, U. S. Dept. Agr., 1896, p. 9; Fourth Annual Report, Maryland Exp. Sta., 1891, p. 258; Bul. No. 4, Weather Bureau, U. S. Dept. Agr. (1892), p. 80; See also Wiley, Principles and Practices of Agricultural Analysis I, 1894, p. 171.

[g] Phys. Rev., **2**, 241 (1895).

[h] Neues Jahrb. f. Mineral. II, p. 147, 1893; abstr., Forsch. Geb. Agr. Phys., **18**, 76 (1895).

[i] Landw. Vers.-Stat., **45**, 137 (1894); abstr., Forsch. Geb. Agr. Phys., **18**, 78 (1895).

Matthews[a] has suggested that the precipitation of colloids by electrolytes is brought about by an alteration in the surface energy of the colloid. The suspending power of the solvent has been correlated with its dielectric constant. Buckingham,[b] however, has shown experimentally that this suspending power, while parallel with the dielectric constant, shows variations of a totally different order of magnitude. Many cases are known in which the flocculation and suspension of particles, bacteria, etc., alternate as the concentration of the solute is increased.[c] This recurrence of flocculation and suspension[d] puts in doubt the hypothesis that suspended particles settle because their charges are neutralized by the ions about them. Buxton and Shaffer[e] have suggested that this precipitation may be analogous to the phenomenon of "salting out," in which a new distribution of the components between solid and liquid phases in the colloidal suspension takes place. In other papers Teague and Buxton[f] have investigated the migration of suspended particles under the influence of electrical stress and found that the direction in which the suspension migrates depends upon the concentration of the electrolyte, and, indeed, alternates as the suspension or flocculation alternates. They suggest the possibility that this alternation may be due to a decrease in the absorptive power of the suspended particles in more concentrated solutions.

Hilgard has given considerable attention to the subject of sedimentation, especially in his method for the mechanical analysis of soils. He has also studied the effect of different salts, alkalies, and acids upon the physical structure of the soil, recognizing the effect of these agents upon sedimentation. His latest statement concerning the formation of soil crumbs is of interest: "When land is plowed in the proper moisture condition, the crumbs or floccules are held together by the surface tension of the capillary films (menisci) of water at the points of contact. In the case of sands, the crumbs will collapse into single grains whenever the water films evaporate, unless some cementing substance was dissolved or suspended in the water. Lime carbonate is one of the substances most commonly found permanently cementing the floccules; hence the ready tillage of most calcareous soils, and especially the loose texture of the 'loess' of the western United States and of Europe and Asia. In these deposits we find sandy and silt aggregates or concretions ranging from 10 or more inches in length (loess puppets) to microscopic size, held together by lime carbonate, but collapsing into silt and sand when the material is treated with acid so as to dissolve the cement. The rough surface of these aggregates, gripping into each other, explains the stability of the steep loess cliffs in the United States, as well as in northeastern China, as observed by Von Richtofen and Pumpelly."[a]

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[a] Am. Jour. Physiol., **14**, 203 (1905).

[b] Trans. Am. Elec.-Chem. Soc., **9**, 261 (1906).

[c] Bechhold, Zeit. phys. Chem., **48**, 385 (1904).

[d] With regard to the protecting action of gelatine and other substances upon the colloidal suspensions, reference may be made to Bredig, Anorganische Fermente (1901).

[e] Zeit. phys. Chem., **57**, 47 (1906).

[f] Ibid., **57**, 64, 76 (1906); **60**, 469, 489 (1907); **62**, 287 (1908).

Mayer,[b] starting from the well-known settling of muddy water by addition of common salt, divides the salt solutions into two classes: (1) those which behave like distilled water, allowing the soil particles to settle regularly according to their diameters and specific gravities; (2) those solutions in which the precipitate forms a mass of cohering flocs, the neighboring particles showing a tendency to hold together. He places hydrochloric acid, nitric acid, sulphuric acid, their salts, fixed alkalies ($NaOH$, KOH, $LiOH$), and ammonia in the first class. Alkali sulphates have only a slight tendency to promote sedimentation. Lime water precipitates the suspension of soil even better than fixed alkalies, while powdered calcium carbonate mixed with the soil before stirring with water has no effect upon the rate of settling.

Mayer also showed that sedimentation is not perceptibly affected until the concentration of solution added reaches a fairly definite per cent. The percentages at which precipitation just takes place are for the following solutes: Soap, 2.5; ammonia, 2.5; neutral sodium phosphate, 2.0; phosphoric acid, 0.8; potassium hydroxide, 0.56; sodium sulphate, 0.4; calcium hydroxide, 0.08; sulphuric acid, 0.025. The soil used was a fine clay from Iowa washed free of carbonates by hydrochloric acid. He showed that a soil subjected to percolation by distilled water at constant pressure allows the liquid to pass through at a constantly decreasing rate. This decrease is produced by packing and by clay particles lodging in the minute soil channels. When a salt solution belonging to his second class—i. e., one capable of precipitating the soil from suspension in water—is passed through a soil already washed and well packed down by percolation, an increase in the rate of flow is observed. He confirmed this phenomenon for sodium chloride and calcium hydroxide and, furthermore, showed that on washing out by percolation the salt absorbed by the soil during its contact with salt solution the rate of flow was very greatly reduced. This phenomenon has been fully confirmed in this laboratory[c] for potassium carbonate solutions passing through Galveston clay, Marshall silt loam, Hagerstown loam, and

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[a] Hilgard, Soils, p. 110 (1906).

[b] Forsch. Geb. Agr. Phys., **2**, 251 (1879).

[c] See page 94; also Cameron and Patten, Jour. Am. Chem. Soc., **28**, 1645 (1906); also Hissink, Chem. Weekblad, **4**, 663 (1907).

Norfolk sand. As a practical application of this sedimentation effect produced by salts, Mayer suggests first that lands flooded by sea water may suffer a deterioration in their physical condition on being again drained. This close packing of the soil would be likely to appear in the second year after flooding rather than in the first. He thinks, too, that the packing of the soil and consequent reduction of air space and ventilation facilitates the reduction of iron sulphate to hydrogen sulphide, or its analogues, especially in alkali soils. As land flooded by sea water, and thus put into dense condition, was not improved by use of lime, he suggests as a last resort that the land be left fallow, subject to freezing and thawing and to the action of turned-under green manure, such as natural plant growth. He points out most strongly the injury to the mechanical structure of a soil rich in clay produced by repeated fertilizing with potassium nitrate. A soil forced in this manner at first gives fine crops, then shows a sudden drop, which can not be corrected by simple addition of all the standard fertilizers. The soil is ruined mechanically for a long time. One of the reasons for this is that the nitrates, like the chlorides, are comparatively easily washed from the soil, and the salt being removed the soil grains pack down in a single-grain condition very hard to overcome. Swaving[a] likewise found that soils flooded by sea water were greatly injured in their physical condition, although not enough salt was absorbed to injure plants.

Fickendey[b] states that the precipitation of a suspension of a natural clay soil requires a much higher concentration of alkalies than is necessary to flocculate a kaolin suspension. He explains this as due to the protective action exercised upon the soil particles by the humic acids which go into the solution when the soil is treated with alkalies and alkali carbonates. Artificial humic acids can likewise restrain precipitation, though less strongly than the humus products of the soil. Tannin also prevents sedimentation, while starch has no perceptible effect. Pure gelatine without addition of electrolyte exerts a precipitating effect upon kaolin suspensions, which increases with the gelatine concentration up to a maximum and then drops considerably. Addition of alkalies to the gelatine solution displaces this maximum speed of settling toward the side of low gelatine concentration; but in acid solution this maximum appears nearer the region of concentrated gelatine solutions and is sharply defined. These observations are taken as giving new light upon the manurial efficiency of lime, in that it precipitates the humic acids of the soil, thus removing substances which tend to maintain the soil in a single grain condition, and enables the soil grains to flocculate and assume open physical condition.

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[a] Landw. Vers.-Stat., **51**, 463 (1898-99).

[b] Jour. Landw., **54**, 343 (1906).

EFFECT OF ABSORPTION UPON WATER-HOLDING POWER OF SOILS.

Van Bemmelen[a] and others have set forth the relation between the absorptive power of a finely divided solid and the quantity of water retained by the individual particles within their own bodies. But in addition to this imbibition effect, soluble material held in concentrated form upon the surface of powder grains materially alters the quantity of solution which this powder can retain in the space between grains after settling from suspension in the given solution.

Wollny[b] has shown that from every standpoint the single grain soil is inferior to a flocculated soil as regards its moisture content and conservation, as well as in respect to aeration.

Ulreich[c] gives data on the influence of various hydroxides, carbonates, phosphates, sulphates, nitrates, and chlorides upon the water content of soils. He concludes from his data that the different hydroxides and salts, in a considerable degree, but in different direction, exercise an influence upon the water-retaining power of the soil. According to their action they may be brought into three groups, of which the first comprises those compounds which produce a lowering of the water capacity of the soil, i. e., hydroxides and carbonates of the alkalies as well as phosphates. A second group includes those salts which appear to be almost without influence upon the retention of water; these are the sulphates. In a third class are the compounds such as nitrates, chlorides, and calcium hydroxide, which increase the water capacity of the soil. He also compares the effect of Knop's nutrient solution[d] with that of lime and obtains similar results with all the soils tried. The Knop solution increased the water capacity of the soil, as would be expected from the preponderance of nitrates and chlorides. This effect is greater as the concentration of the solution increases, so far as his experimental data go, save in the case of gypsum, where the soil held the same volume of solution at 0.1 per cent $CaSO_4$ as at 0.5 per cent, and showed a very slight decrease in water content when a 1 per cent solution was used.

The interdependence of absorption, flocculation, and physical condition of soils is shown in a series of preliminary experiments carried out by Mr. J. O. Belz. The quantity of solute retained in the soil spaces after settling from a given solution was determined by measuring the height of the soil surface. Since the true volume of the soil grains is a constant, the volume of water held in the capillary spaces may be calculated from this height. Susquehanna clay appears to retain a maximum volume of liquid in potassium hydroxide solution when the concentration is near 0.01 N. This same soil retains more of 0.1 N ammonia solution than of other concentrations used. In both these cases the definite location of the concentration giving maximum open structure remains to be determined, but its existence is assured. With sulphuric acid the volume of solution in the pore spaces is greater as the concentration of acid in solution increases up to 0.1 N, the strongest solution used. Susquehanna clay and quartz flour retain less of distilled water in their capillary spaces than of solution, while Hagerstown loam holds more of distilled water—which, of course, becomes a soil solution proper to that soil—than of dye solution; yet this soil, too, shows a maximum after the first quantities of dye have been absorbed. Calcium nitrate solution (200 c. c.) was shaken up with 25 grams of Sharkey clay and allowed to settle three days before taking the reading. The clay retained a greater volume of the 0.01 N solution than of the other solutions higher and lower in concentration.

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[a] Zeit. anorg. Chem., **23**, 112 (1900).

[b] Forsch. Geb. Agr. Phys., **16**, 406 (1893); **18**, 63 (1895); Puchner, Ibid., **19**, 1 (1896).

[c] Ibid., **19**, 52 (1896).

[d] This solution contains KH_2PO_4, $MgSO_4$, KNO_3, NH_4Cl, in equal parts by weight, with 4 parts $Ca(NO_3)_2$.

Table XI gives the results of a number of experiments also carried out by Mr. Belz. The solutions used were 0.5 and 0.1 normal, except lime, where the concentration was calculated on a basis of pounds per acre. Fifty grams of Susquehanna clay were shaken up with 150 c. c. of solution and allowed seven days in which to come to equilibrium. The results show that the solute used, and in particular its concentration in the soil and in the solution, determines the volume of solution which the soil can retain in its capillary spaces. It is to be remembered that the original concentrations given in Table XI have changed, since in each case the soil has abstracted a goodly quantity of solute from the solution.

TABLE XI.—*Volume of solution retained by Susquehanna clay on settling from various solutions.*

[50 grs. soil + 150 c. c. solution.]

Solute.	(1) Volume of solution in soil.[a]	(2) Volume of solution in soil.	(1) Difference in volume over distilled water check.	(2) Difference in volume over distilled water check.
	0.5 normal solution.	0.1 normal solution.		
	C. c.	*C. c.*	*C. c.*	*C. c.*
Distilled water	75.4	....	....	....
Lime (1)	72.0	....	−3.4	....
Lime (2)	59.1	....	−16.3	....
$(NH_4)_2CO_3$	104.6	105.6	29.2	30.2
K_2CO_3	91.4	126.4	16.0	51.0
Na_2CO_3	128.1	131.9	53.2	66.5
H_2SO_4	120.9	101.2	45.5	25.8
K_2SO_4	110.4	117.7	35.0	42.3
Na_2SO_4	126.1	113.8	50.7	38.4
$(NH_4)_2SO_4$	111.3	117.6	35.9	42.2
Na_2HPO_4	126.7	128.7	51.3	53.3
$(NH_4)_2HPO_4$	118.1	125.8	42.7	50.4
K_2HPO_4	108.7	121.2	33.3	47.8
$Ca(NO_3)_2$	60.5	69.4	−14.9	−6.0
$NaNO_3$	97.7	69.8	22.3	−5.6
KNO_3	80.4	70.1	5.0	−5.3
$(NH_4)NO_3$	73.0	89.4	7.6	14.0

[a] The volume of the air-dry soil is 41.1 c. c. for 50 grams.

Column 1 = 1,000 pounds per acre. Column 2 = 500 pounds per acre.

Increase in lime increases the volume of solution in the soil, and the same is true for sodium, potassium, and ammonium nitrates, sulphuric acid, and sodium sulphate; but the other salts studied show the reverse, the volume of solution retained by the soil being greater for lower concentrations. This apparent lack of agreement of the effect of various solutes is due to the fact that each solution has its own particular concentration for which the soil in contact with it will assume a maximum open structure.

The following experiments were undertaken to establish a relationship between the quantity of substance absorbed by the particles and the volume of solution which they can retain in the spaces between particles when the aggregate of grains is allowed to settle out of solution and pack down. Consequently in addition to determining the concentration of the solution remaining above the quartz flour, as shown in Table IV, its volume was measured; that is, the volume of liquid which could be drained off from the quartz after the bottles containing the system had been centrifuged at high speed for about ten hours and then allowed to stand some six weeks upon the shelf. As the quartz had settled into a compact mass in every bottle, the volume of liquid remaining above the quartz could be poured off cleanly and measured to within less than 0.3 c. c. The water added to each sample of quartz may be considered to be in three conditions—absorbed water, that held in the capillary spaces, and free water. The free water was directly determined, and the absorbed water has been determined for the same samples of quartz;[a] consequently the water held in the capillary spaces may be estimated by difference.

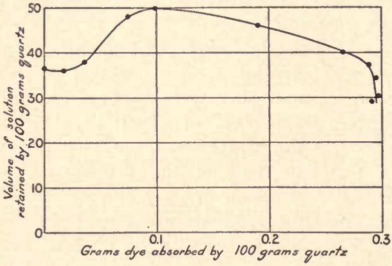

FIG. 2.—Curve showing the relation of the quantity of gentian violet dye absorbed by quartz flour to the volume of solution retained by the quartz after settling.

Table XII shows the volume of solution retained in the capillary spaces of 100 grams of quartz flour for different quantities of gentian violet dye absorbed by the quartz grains.[b] The corresponding concentration of each dye solution used has been given above in Table IV. The curve given in figure 2 is plotted from Table XII, using the grams of dye absorbed by 100 grams of quartz flour as abscissas and the volume of solution retained by the quartz in the capillary spaces as ordinates. The maximum of liquid is held by the quartz between its particles when about one-third of the dye which can be taken up by the grains has been adsorbed.

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[a] Patten and Gallagher, Bul. No. 51, Bureau of Soils, U. S. Dept. Agr., 1907.

[b] Trans. Am. Electrochem. Soc., **10**, 67 (1906).

TABLE XII.—*Volume of solution in the capillary spaces of quartz flour when various quantities of gentian violet have been absorbed.*

Dye absorbed by 100 grams of the quartz flour.	Volume of solution retained by 100 grams quartz flour.	Dye absorbed by 100 grams of the quartz flour.	Volume of solution retained by 100 grams quartz flour.	Dye absorbed by 100 grams of the quartz flour.	Volume of solution retained by 100 grams quartz flour.
Gram.	*C. c.*	*Gram.*	*C. c.*	*Gram.*	*C. c.*
0.000	36.5	0.0984	50	0.295	34
.017	36	.1991	46	.297	30
.036	38	.266	40	.293	29
.074	48	.289	37	.290	29

Similar measurements, using Hagerstown loam soil, are given in Table XIII. The maximum pore space for this soil evidently is attained with no dye present, and as the quantity of dye absorbed by the soil grains increases the soil settles together and retains less and less liquid, then expands again as it takes on more dye, till when 1 gram of dye is absorbed by 100 grams of soil, 57 c.c. of solution remains in the pore spaces. Further increase in the dye absorbed decreases the volume of solution in the capillary spaces. With 2 grams of dye to 100 grams of soil 45 c.c. of solution is held. This is 26.2 per cent less capillary liquid than the undyed soil retained, and 21 per cent less than is held by the soil containing 1 gram absorbed dye per 100 grams of soil. Marshall silt loam also shows this same volume effect, as indicated by the data in Table XIV.

TABLE XIII.—*Volume of solution in the capillary spaces of Hagerstown loam when various quantities of gentian violet have been absorbed.*

Dye absorbed by 100 grams soil.	Volume of solution retained by 100 grams soil.	Dye absorbed by 100 grams soil.	Volume of solution retained by 100 grams soil.
Gram.	*C. c.*	*Grams.*	*C. c.*
0.0	61	1.0	57
.20	56	1.495	50
.40	54	1.98	45
.60	55		

TABLE XIV.—*Volume of solution in the capillary spaces of Marshall silt loam when various quantities of gentian violet have been absorbed.*

Dye absorbed by 100 grams soil.	Volume of solution retained by 100 grams soil.	Dye absorbed by 100 grams soil.	Volume of solution retained by 100 grams soil.
Grams.	*C. c.*	*Grams.*	*C. c.*
0.50	47	3.7+	39
1.00	50	3.7+	37
1.50	47		

TABLE XV.—*Volume of solution in the capillary spaces of quartz when various quantities of eosine have been absorbed.*

Eosine absorbed by 100 grams quartz.	Volume of solution retained by 100 grams.	Eosine absorbed by 100 grams quartz.	Volume of solution retained by 100 grams.
Gram.	*C. c.*	*Gram.*	*C. c.*
0.00000	42	0.0348	29
.00135	30	.42	29

The effect of eosine dye upon the volume of solution which quartz flour can retain in its capillary space serves to further correlate flocculation and absorption with the physical condition of a soil. Considering the data given in Table XV, we see that the absorption of 0.00135 per cent of the dye reduces the volume of liquid retained from 42 c. c. to 30 c. c. and that further absorption of dye has very little effect upon the volume of liquid in the pore spaces. Turning back to Table XII and figure 2, it appears that this volume, 30 c. c., is the same as the lowest volume of liquid held by 100 grams of quartz flour when its absorption capacity for gentian violet is reached. These suspensions of quartz flour in eosine solution were allowed to settle for over five weeks, and when the supernatant liquid was poured off in each case quartz particles were still suspended in the liquid, although the bottles had been subjected to rapid centrifugal treatment for two days at the beginning of this period. The volume of quartz flour not yet settled from the eosine solutions was insufficient to affect the accuracy of the measurements on the volume of solution retained by the compact mass of quartz at the bottom of each bottle. It shows, however, that the eosine dye had deflocculated the quartz particles and that the smallness of the volume of solution, 30 c. c., retained by the settled quartz flour is in all likelihood due to the fact that these particles settled from suspension as single grains or in small aggregates, i. e., deflocculated. The quartz suspensions in gentian violet solution were very noticeably flocculated, save for the high concentrations, where long-continued centrifuging was necessary to clear the solution of suspended quartz particles. And reference to figure 2 will show that the volumes of dye solution retained by quartz are parallel to the condition of the system as regards flocculation, the small volume, 30 c. c., being held by quartz when the concentration of the solution in gentian violet dye is high.

It is evident, then, that the quantity of soluble material absorbed by a soil has a marked influence upon the arrangement of the soil grains into aggregates. Different salts have widely different effects upon the soil structure, and the particular strength of soil solution for which the formation of soil aggregates is a maximum is not the same for each salt. Consequently where mixed solutions, such as those which exist in soils under field conditions, are used it will require a vast deal of experimental work before a prediction can be made as to the exact effect of a particular solution upon the physical condition of a soil.

Nevertheless the above treatment of the effect of absorbed material upon the physical condition gives a good understanding of the agencies at work in the formation of soil structures. And when this point of view is coupled with definite data, such as that in Tables XI to XV, the probable effect of a fertilizer or corrective upon the physical condition of a soil may be given, as well as its addition of mineral plant nutrients. This is especially needed since some fertilizers rich in mineral plant nutrients are ultimately injurious to the physical condition of a soil in a very high degree.

PERCOLATION STUDIES.

RECLAMATION OF BLACK ALKALI SOIL BY LEACHING.

The reclamation of soils containing "black alkali," or soluble carbonates, presents unusual difficulties. These difficulties are due in large part to the fact that soils generally show decidedly higher absorptive powers toward bases present in alkaline solutions than when the solutions are neutral or acid,[a] and that the presence of hydroxides or carbonates of the alkalies frequently induces a "puddling" of the soil, preventing a thorough penetration by water and subsequent removal of the water, with its dissolved contents, by drainage. The latter effect was subjected to a laboratory investigation by Cameron and Patten,[b] using two "black alkali" soils which were in process of reclamation.[c] One, a sample from North Yakima, Wash.,[d] was from the surface 8 inches of the experimental tract north of Wide Hollow Creek. The second sample,[e] from the Toft-Hansen tract at Fresno, Cal., was from the upper 8 inches of soil in a spot plainly showing "black alkali" at the surface. When collected there were only a few scattering spears of grain on this spot, although all about it the grain had made a good stand. When the crust formed by the "alkali" was broken, grain was found which had sprouted but had not been able to push through the crust. A calcium carbonate hardpan occurred about 3 feet below the surface, but was also found at the same depth in adjoining fields on which there was a good stand of barley.

Chemical analyses of the water-soluble salts in these samples by the conventional method[f] of digesting the sample with five times its weight of water gave the results shown in Table XVI. It will be observed that both samples were of the same type of alkali soils, containing, besides the soluble carbonates, notable quantities of sodium sulphate, with much less amounts of other sulphates and chlorides.

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[a] See Bul. No. 30, Bureau of Soils, U. S. Dept. Agr., 1905.

[b] Jour. Am. Chem. Soc., **28**, 1639 (1906).

[c] Bul. No. 42, Bureau of Soils, U. S. Dept. Agr., 1907.

[d] Sample No. 14413, Bureau of Soils collection.

[e] Sample No. 14402, Bureau of Soils collection.

[f] Bul. No. 18, p. 65, Bureau of Soils, U. S. Dept. Agr., 1901.

From the mechanical analyses of these samples (Table XVII), together with their field properties, both the Yakima and Fresno soils would be classified as fine sandy loams.

TABLE XVI.—*Water-soluble constituents in soils from North Yakima, Wash., and Fresno, Cal., extracted by digesting one part of soil with five parts of water.*

Constituent.	North Yakima.	Fresno.	Constituent.	North Yakima.	Fresno.
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
Ca	Tr.	Tr.	Cl	0.03	0.03
Mg	0.02	Tr.	HCO_3	.27	.16
Na	.24	0.13	CO_3	.10	.02
K	.03	.02			
SO_4	.18	.09	Total	.87	.45

TABLE XVII.—*Mechanical analyses of soils from North Yakima, Wash., and from Fresno, Cal.*

Conventional name.	Diameter.	North Yakima.	Fresno.
	mm.	*Per cent.*	*Per cent.*
Fine gravel	2 to 1	Tr.	0.1
Coarse sand	1 to 0.5	1.3	2.1
Medium sand	0.5 to 0.25	2.5	3.7
Fine sand	0.25 to 0.01	12.8	24.7
Very fine sand	0.01 to 0.05	21.2	33.6
Silt	0.05 to 0.005	48.6	29.5
Clay	0.005 to 0	13.5	6.2

EXPERIMENTAL METHODS.

The method of percolation was essentially the same as that employed by Schreiner and Failyer,[a] with the exception that a constant water pressure was maintained instead of keeping the rate of percolation constant. One hundred grams of soil were placed in a paraffined brass tube fitted below with a short section of a Pasteur-Chamberland filter tube, and distilled water allowed to percolate through the soil under a constant water pressure of 199 cm., or 6.5 feet.

The volume of each percolate was measured, its electrical conductivity taken with a field bridge,[b] and its time of flow recorded. Normal carbonates (CO_3) and bicarbonates (HCO_3) were then determined volumetrically with standard acid potassium sulphate solution and the chlorine titrated with tenth normal silver nitrate solution, using potassium chromate as indicator. Sulphates were not determined, because the amounts here involved are too small to have any great agricultural significance and the analytical difficulties in handling quantities of this magnitude would be unjustifiably great.

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[a] Jour. Phys. Chem., **10**, 239. 361 (1906). Bul. No. 32, Bureau of Soils, U. S. Dept. Agr., 1906.

[b] Bul. No. 15, Bureau of Soils, U. S. Dept. Agr., 1899, p. 15.

RESULTS WITH SOIL FROM NORTH YAKIMA.

The data obtained with the Yakima soil are given in Table XVIII. The first column gives the time during which percolation has been progressing; the second column, the total volume of percolate; the third column, the conductivity of the successive percolates, at 25° C., expressed in reciprocal ohms multiplied by 1,000, which may be converted to "specific conductivity" by multiplying by the cell factor, 3.57. The next three columns give concentrations in the successive leachings, and the last three columns show the total amounts of the several constituents removed from the soil.

TABLE XVIII.—*Extraction of alkali salts from North Yakima soil by leaching.*

Time.	Volume of percolate passed.	Conductivity of successive portions of percolate $\times 10^3$. T = 25° C.	Concentration of successive portions of percolate in ppm. of solution.			Total quantity of constituents leached from 100 grams of soil.		
			CO_3.	HCO_3.	Cl.	CO_3.	HCO_3.	Cl.
Hours.	*C. c.*	*Ohms.*	*Ppm.*	*Ppm.*	*Ppm.*	*Gram.*	*Gram.*	*Gram.*
48	37	....	84	1,160	193	0.00304	0.0424	0.00715
120	101	....	196	1,586	110	.0156	.1439	.01420
216	170	5.76	171	753	152	.0274	.1962	.02470
264	242	3.62	223	406	4	.0433	.2252	.02498
312	312	4.07	168	445	2	.0550	.2563	.02512
360	383	3.98	128	403	3	.0641	.2849	.02533
432	473	3.38	89	385	4	.0722	.3199	.02569
480	539	2.94	64	388	4	.0764	.3451	.02595
558	629	2.80	73	321	1	.0829	.3740	.02607
726	739	2.49	73	263	0.7	.0909	.4029	.02615
778	829	2.17	73	218	Tr.	.0974	.4225	....
827	917	2.04	67	221	....	.1034	.4420	....
873	992	1.90	78	158	....	.1093	.4538	....
940	1,097	1.71	78	130	....	.1173	.4675	....
988	1,184	1.77	59	170	....	.1219	.4823	....
1,065	1,314	1.63	42	185	....	.1273	.5065	....
1,114	1,398	1.51	34	164	....	.1301	.5203	....
1,163	1,485	1.33	22	170	....	.1322	.5352	....
1,210	1,562	1.24	27	145	....	.1343	.5470	....
1,259	1,642	1.03	22	127	....	.1361	.5583	....
1,306	1,716	1.03	6	139	....	.1365	.5683	....
1,378	1,831	1.00	8	130	....	.1372	.5733	....
1,443	1,951	.91	11	109	....	.1385	.5864	....
1,499	2,050	.93	11	115	....	.1396	.5978	....
1,566	2,138	.83	8	163	....	.1404	.6069	....
1,614	2,216	.74	6	94	....	....	.6142	....
1,665	2,306	.71	6	85	....	....	.5214	....
1,711	2,378	.68	6	79	....	....	.6271	....
1.785	2,490	.61	6	73	....	....	.6353	....
1,836	2,586	.59	0	79	....	....	.6429	....
1,884	2,673	.59	0	67	....	....	.6487	....
1,932	2,768	.51	0	67	....	....	.6551	....
2,004	2,908	.45	0	67	....	....	.6645	....
2,076	3,028	.48	0	61	....	....	.6718	....
2,148	3,148	.43	0	55	....	....	.6784	....
2,340	3,378	....	0	51	....	....	.6900	....
2,460	3,583	....	0	47	....	....	.6996	....
2,580	3,813	.51	....	42	....	....	.7093	....
2,772	4,088	....	....	42	....	....	.7209	....
2,887	4,276	....	....	39	....	....	.7283	....
3,007	4,526	.48	....	36	....	....	....	....
3,125	4,741	.49	....	36	....	....	....	....
3,246	4,941	.49	....	33	....	....	....	....
3,391	5,201	.44	....	24	....	....	....	....
3,583	5,528	.53	....	9	....	....	....	....
3,803	5,958	.39	....	18	....	....	....	....
3,899	6,142	.42	....	18	....	....	....	....

An inspection of the results presented in Table XVIII shows that while the water passing through the soil is kept under a constant head the rate of percolation is not constant, but varies somewhat from time to time. The first water entering the dry soil runs through quite rapidly, but as soon as the soil becomes saturated it moves much more slowly. Variations in the rate of percolation are subsequently observed, due undoubtedly in some cases to "channeling" in the soil, in some cases probably to "silting up" of channels, and in other cases partly to the fact that as the percolation proceeds the strongly deflocculating action of the alkali diminishes as its quantity decreases, so that the soil behaves as if it suffered a change in texture as well as in structure. For these reasons the concentrations of the successive portions of the percolates, as evidenced by the conductivity as well as by the analyses, do not show a *regularly* progressive change, although on the whole the concentrations become lower and lower as percolation proceeds. These results are in harmony with many field observations where it has been found that the concentration of a drainage water may vary over quite a wide range, depending upon the rate at

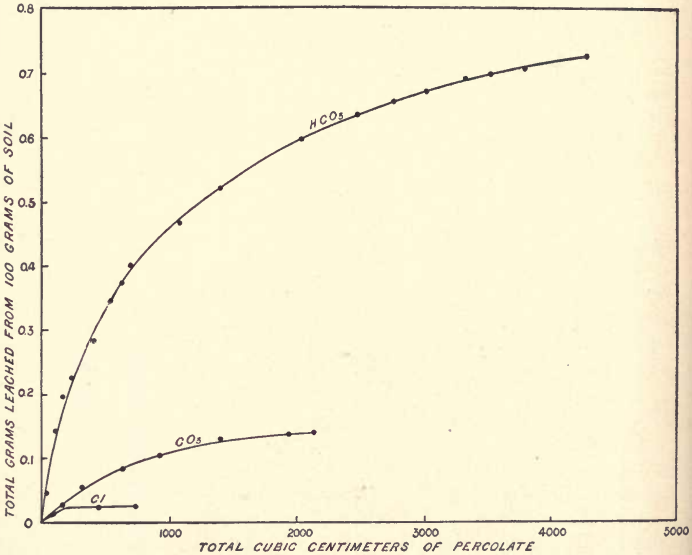

FIG. 3.—Curve showing the total quantities of carbonates, bicarbonates, and chlorine removed by percolating North Yakima black alkali soil with distilled water.

which the applied water moves through the soil and upon the length of time of contact between the water and soil, since considerable time is necessary for equilibrium to result between the salts dissolved and those remaining in the soil.[a]

In the present case chlorides had practically disappeared after 778 hours, when 829 c. c. of water had passed through the soil. Normal carbonates failed to appear in the percolate after 1,614 hours, when 2,216 c. c. of solution had passed. This does not mean, however, that no normal carbonates remained in the soil, for, as has been previously shown in this laboratory,[b] dilution of a normal carbonate causes a change with formation of bicarbonate. It is certain that after 1,614 hours the amount of normal carbonates in the solution has been reduced to a point below that dangerous to plant growth. The alkali, in the form of bicarbonates, however, continued to be leached from the soil after percolation had proceeded for 120 days and a total volume of over 4,200 c. c. had passed through the soil. The results are readily seen in figure 3, where the abscissas are total volume of percolate and the ordinates total grams of the several constituents removed from the soil. The curves are all asymptotic. In the case of the chlorides and normal carbonates, as noted above, the amounts in the successive portions of percolate soon become too small to determine accurately; but in the case of the bicarbonate, amounts could still be readily determined, while the run of the figures in the table and the shape of the curve show that at the termination of the experiment the amount in the successive portions of percolate was slowly diminishing. This is brought out more

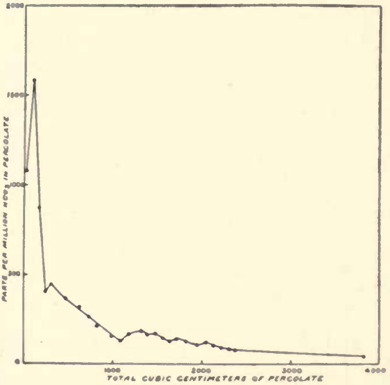

FIG. 4.—Curve showing the quantity of bicarbonate in solution in the successive percolates when North Yakima black alkali is leached with distilled water.

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[a] Bul. No. 33, Bureau of Soils, U. S. Dept. Agr., 1906, and Jour. Am. Chem. Soc., 28, 1229 (1906).

[b] Bul. No. 18, Bureau of Soils, U. S. Dept. Agr., 1901; Jour. Phys. Chem., 5, 537 (1901).

clearly in figure 4, in which the ordinates represent the concentrations in parts per million in successive portions of the percolate. This result is analogous to former leaching experiments made in this laboratory. An inspection of the results for bicarbonates shows, moreover, that if the first few observations be disregarded the leaching curve is described with fair accuracy by the equation

$$\frac{dy}{dv} = K(A - y)$$

proposed by Schreiner and Failyer.[a]

RESULTS WITH SOIL FROM FRESNO.

In working with the Fresno sample the same experimental difficulties were encountered as with the Yakima sample, in that changes in flocculation and channeling materially affected the rate of leaching. In Table XIX are given the rates of leaching during the earlier part of the experiment. The results are more clearly shown in figure 5. It is seen that at first there is a rapid fall in the rate, and then as percolation proceeds, with the formation of channels and an increase in the flocculation due to the partial removal of the alkali, there is an increase in the rate of percolation, becoming quite regular after about 300 c. c. have passed through the soil. It is believed that these changes in the physical condition of the soil as affecting percolation in these experiments are very helpful in showing what may be expected in field practice, although it must be remembered that the intermittent leaching to which the soil is sub-

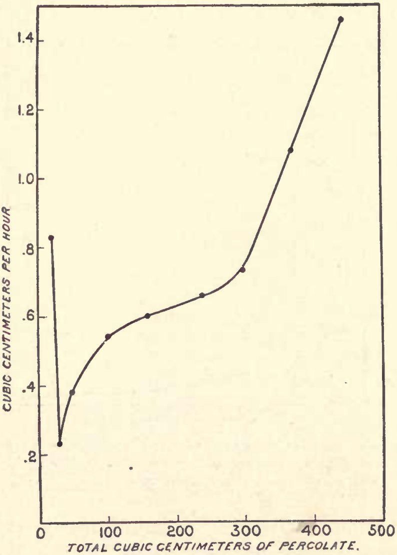

FIG. 5.—Curve showing the progressive change in the rate of percolation as the soluble salts are extracted from Fresno black alkali soil by distilled water.

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[a] Bul. No. 32, Bureau of Soils, U. S. Dept. Agr., 1906.

jected in the field should be more effective than the laboratory results, at least in so far as respects the volume of water required.

In Table XX are given the data obtained from the leachings of the Fresno soil, which are also shown in figures 6 and 7.

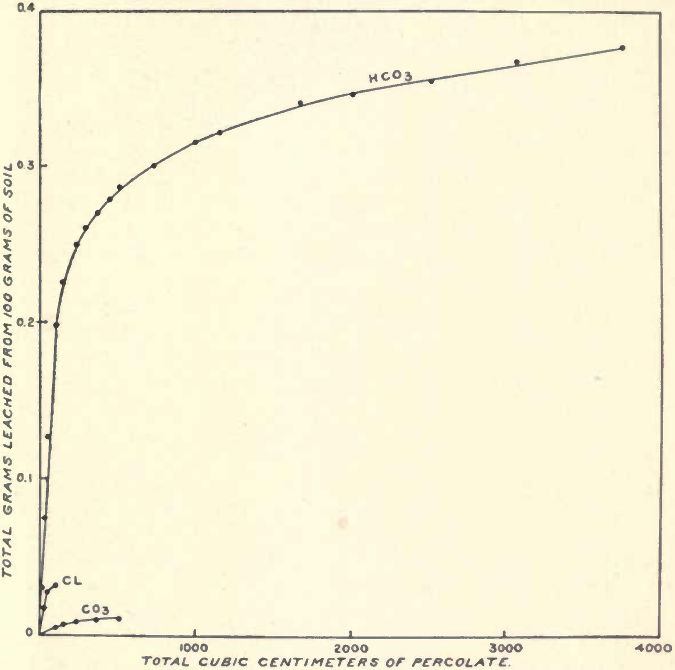

FIG. 6.—Curve showing the total quantities of carbonates, bicarbonates, and chlorine removed by percolating Fresno black alkali soil with distilled water.

TABLE XIX.—*Rate of leaching through soil from Fresno.*

Total percolate.	Quantity per hour.	Total percolate.	Quantity per hour.	Total percolate.	Quantity per hour.
C. c	*C. c.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*
20	0.83	101	0.54	295	0.73
31	.23	159	.60	368	1.08
49	.38	238	.66	443	1.46

TABLE XX.—*Extraction of alkali salts from Fresno soil by leaching.*

Time.	Volume of percolate passed.	Conductivity of successive portions of percolate × 10^3. T=25° C.	Concentration of successive portions of percolate in p.p.m. of solution.			Total quantity of constituents leached from 100 grams of soil.		
			CO_3.	HCO_3.	Cl.	CO_3.	HCO_3.	Cl.
Hours.	*C. c.*	*Mhos.*	*P.p.m.*	*P.p.m.*	*P.p.m.*	*Gram.*	*Gram.*	*Gram.*
24	20	....	....	1,514	352	....	0.0303	0.0070
72	31	....	....	4,125	961	....	.0757	.0176
120	49	....	....	2,860	489	....	.1268	.0264
216	101	7.87	81	1,370	101	0.0042	.1981	.0317
312	159	3.31	45	475	0	.0068	.2256	....
432	238	2.37	23	297	....	.0086	.2489	....
510	295	1.603	12	206	....	.0092	.2606	....
578	368	1.243	12	137	....	.0100	.2706	....
630	444	.842	3	112	....	.0102	.2791	....
679	514	.680	1	105	....	.0103	.2865	....
724	572	.59	0	79	....	....	.2911	....
791	656	.52	....	73	....	....	.2972	....
839	724	.53	....	67	....	....	.3017	....
916	833	.49	....	64	....	....	.3087	....
964	912	.401	....	55	....	....	.3131	....
1,014	1,000	.366	....	33	....	....	.3160	....
1,061	1,083	.361	....	33	....	....	.3187	....
1,110	1,162	.351	....	33	....	....	.3214	....
1,157	1,230	.376	....	43	....	....	.3242	....
1,229	1,345	.417	....	42	....	....	.3291	....
1,301	1,459	.400	....	42	....	....	.3340	....
1,357	1,558	.370	....	37	....	....	.3376	....
1,424	1,667	.334	....	27	....	....	.3406	....
1,472	1,744	.307	....	21	....	....	.3422	....
1,523	1,829	.312	....	19	....	....	.3437	....
1,569	1,905	.283	....	15	....	....	.3449	....
1,643	2,017	.296	....	12	....	....	.3462	....
1,694	2,104	.293	....	15	....	....	.3475	....
1,742	2,185	.293	....	18	....	....	.3490	....
1,790	2,271	.292	....	18	....	....	.3506	....
1,862	2,393	.235	....	15	....	....	.3524	....
1,934	2,513	.209	....	15	....	....	.3542	....
2,006	2,626	.202	....	15	....	....	.3559	....
2,198	2,856	....	....	17	....	....	.3598	....
2,318	3,061	....	....	18	....	....	.3635	....
2,438	3,291	.362	....	18	....	....	.3677	....
2,630	3,575	....	....	25	....	....	.3745	....
2,745	3,756	....	....	15	....	....	.3773	....
2,865	3,961	.331	....	9	....	....	....	....
2,983	4,126	.311	....	6	....	....	....	....
3,128	4,346	.451	....	6	....	....	....	....
3,272	4,534	.797	....	6	....	....	....	....
3,468	4,796	.566	....	3	....	....	....	....
3,688	5,136	.859	....	3	....	....	....	....
3,780	5,284	.407	....	3	....	....	....	....

COMPARISON OF RESULTS FOR THE TWO ALKALI SOILS.

In general the results for Fresno soil are very similar to those obtained with the heavier soil from Yakima, but, as might reasonably be expected, the soluble salts disappear more rapidly from the lighter soil. It is also worthy of note that in the case of the Fresno soil the curve for chlorides (fig. 6) lies above that for normal carbonates, while the reverse is the case with the Yakima soil (fig. 3); but this is not a case of selective absorption, for the Yakima soil contained, initially, much more of the carbonates than did the Fresno sample, while both contained approximately the same quantities of chlorides. Further, the later leachings are more dilute than in the case of the heavier Yakima soil, indicating that the latter possesses a higher absorptive power.

The leachings from the two soil samples here described have resulted in the removal of larger total quantities of soluble salts than is indicated by the standard method of analysis. The quantity of carbonates removed by the leaching process agrees, within the limits of experimental error, with the amounts found by digesting the soil with five times its weight of water. In the case of normal carbonates the continuous leachings as compared with the digestion used in the analytical procedure, showed slightly more in the Yakima soil and somewhat less in the Fresno sample. The differences are, however, so small as to be quite possibly ascribed to analytical errors. But it should be remembered that the addition of much water has the effect of converting a part of the normal carbonates into bicarbonates, and it is in respect to this constituent that the leaching process yields much higher results than does the empirical analytical method, which can not take cognizance of absorption effects. The results on the whole indicate that the empirical procedure with the known inherent defects nevertheless gives a very fair idea of the soluble constituents of the soil where the generally impracticable method of leaching can not be employed.

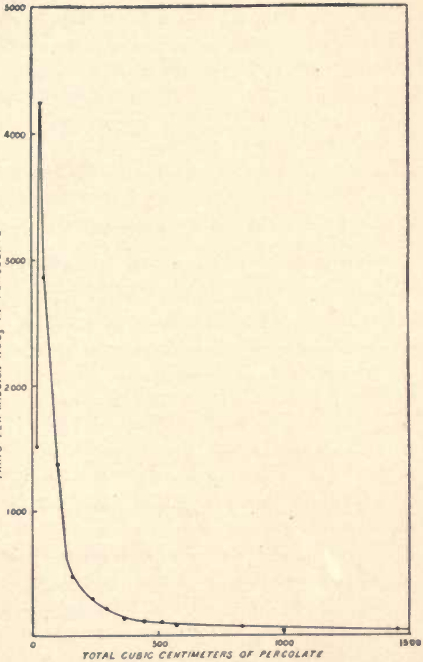

FIG. 7.—Curve showing the quantity of bicarbonate in solution in the successive percolates when Fresno black alkali soil is leached with distilled water.

During the latter half of each percolation experiment the conductivities of the successive percolates show irregular deviations from a fairly constant value, while the titration number for successive percolates slowly diminishes. In the case of the North Yakima soil this mean value of the conductivity, and also the titration numbers, are somewhat higher than for the Fresno soil.

The leaching results presented above indicate the following conclusions: Neutral salts, such as chlorides, in the presence of carbonates are comparatively easy to leach from the soil. With continued leaching of the soils containing "black alkali" there is an increase in the rate at which percolation takes place, due probably to the reduction of the amount of alkali present and to a consequent effect on the physical structure of the soil. With continued leaching there is a comparatively rapid reduction of normal carbonates in the soil water, due in large measure to conversion to bicarbonates. Bicarbonates are rapidly removed at first and then continue to be slowly removed in the soil water in very small quantities, diminishing for an indefinite period. The leaching curves conform fairly well to the rate equation, $\frac{dy}{dv} = K(A - y)$, proposed by Schreiner and Failyer. Soils containing "black alkali" can be reclaimed by leaching (i. e., flooding with underdrainage), but the time and amount of water required is probably much greater than in the case of "white alkali."

EFFICIENCY OF CALCIUM SULPHATE IN REMOVING BLACK ALKALI.

Calcium sulphate has been proposed as a remedy for the injurious effect of black alkali upon growing plants. In order to test the effect of calcium sulphate upon the removal of sodium carbonate and bicarbonate under percolation conditions, four experiments were undertaken. In experiments (1) and (3) of Table XXI, 100 grams of the natural alkali soils from North Yakima, Wash., and from Fresno, Cal., were used. Part of each soil in dry powder (70 grams) was slowly poured into the brass percolation tube and allowed to settle down through the water in it and form a percolation bed. The remainder (30 grams) was meanwhile rubbed up with 10 grams of calcium sulphate and then poured into the tube with the rest of its sample, where it settled, forming a top layer rich in calcium sulphate. Distilled water was then added from time to time, replacing that which passed through the soil. The presence of the calcium sulphate was immediately evident from the rapidity with which the solution passed down through the soil, whereas the untreated natural alkali soils when moistened puddle immediately and in the apparatus used in this work require several feet of water head to produce percolation.

A separate series of experiments, carried out under equilibrium conditions with the North Yakima soil, showed that when the theoretical amount of calcium sulphate required to react with the carbonate and bicarbonate is added and rubbed into the soil, and the soil shaken with water and allowed to settle, the sediment thus obtained occupies a greater volume than that for greater or less additions of the calcium sulphate. This maximum point is as yet not so definitely determined as the above statement might indicate, but nevertheless shows the effect of calcium sulphate upon the *volume* and *openness* of this soil when saturated with water, as it is in the percolation tube. A similar series of experiments with the Fresno soil gave corresponding results, but here the maximum volume of sediment was not reached until *three* times the quantity of calcium sulphate equivalent to the carbonates and bicarbonates in the soil had been added. Experiments (2) and (4) were likewise made with the Yakima and Fresno soils, the experimental conditions being the same as in experiments (1) and (3), save that sodium chloride was added to each soil in sufficient quantity to bring its percentage content up to that of an average black alkali sample from the particular locality to which each soil belongs. This was necessary since these samples proved low in chlorides, and it was desirable to use them in this work because their loss of carbonates and bicarbonates had been already determined under known percolation conditions, and could serve for comparison with this similar series in which calcium sulphate is present.

The sodium chloride was added dry to the alkali soils, rubbed up, water added to make a paste, the soil allowed to dry, and again broken up; calcium sulphate was then worked into the top 30 grams as for experiments (1) and (3).

TABLE XXI.—*Effect of calcium sulphate upon the removal of black alkali by leaching.*

Soil.	Volume of percolate passed.	$CaSO_4$ added.	NaCl added.	Concentration of percolate.			Total constituents leached from 100 grams soil.		
				CO_3.	HCO_3.	Cl.	CO_3.	HCO_3.	Cl.
	C. c.	*Grams.*	*Grams.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*Grams.*	*Grams.*	*Grams.*
North Yakima	30	10		69	656		0.002	0.0197	
	86			0	468		.002	.0459	
	267				193		.002	.0909	
	296				58		.002	.0926	
	334				40		.002	.0936	
	465				39		.002	.099	
	527				39		.002	.1014	
	730				37		.002	.1089	
	807				51		.002	.1148	
	951				40		.002	.1206	
Do	30.5	10	0.75		223	6,560		.0068	0.2002
	45			10	142	4,780	.00015	.0089	.2672
	177			60	182	1,333	.008	.0125	.4427
	230			60	197	42	.0112	.0229	.465
	333			45	91	10	.0158	.0323	.466
	381				76	0		.0360	
	426				47	0	.0158	.0428	.466
Fresno	13.5	10			1,400			.0189	
	34				1,515			.0492	
	144				223			.0738	
	296				46			.0808	
	415				42			.0856	
	573				52			.0938	
	672				49			.0984	
Do	15	10	.335		263	10,640		.0039	.1506
	122			15	136	5,250	.0016	.0185	.7216
	173				53	21		.0202	.7323
	281				44	0		.0250	
	316				43	0		.0265	
	450				45	0	.0016	.0326	.7323

The headings of Table XXI are self-explanatory. Table XXII contains a summary of the most important points brought out in Table XXI and in the leaching experiments on these soils, already given, using only distilled water.

For the North Yakima soil containing gypsum the quantity of carbonates in the successive percolates decreased continually, whereas in the natural alkali soil an intermediate portion of the percolate had the highest content. Furthermore, the concentration of bicarbonate in the percolates from the soil treated with calcium sulphate were many times lower than the corresponding concentration of the percolate from the untreated soil.

Moreover, using distilled water alone 2,490 c. c. were passed before all the normal carbonate was leached; but with calcium sulphate present, all the normal carbonates came out in the first 30 c. c. of percolate, and this volume of liquid is very nearly that required to saturate this soil with water; therefore it is very likely that the calcium sulphate solution from the top layer of soil in the percolation tube did not react with this first percolate to its full extent, but pushed this solution on before it and out of the soil. That some reaction had taken place is shown by the decrease of nearly one-half (43.4 per cent) in the quantity of bicarbonates present in even this first percolate.

Distilled water leached in all 0.7283 gram bicarbonate from the natural soil, while with calcium sulphate present only 0.1206 gram bicarbonate appeared in the filtrate. Using calcium sulphate, only one-tenth of the volume of water was required to reduce the concentration of bicarbonate in the percolate to 40 parts per million. Experiment 2 indicates that the presence of sodium chloride in quantity does not materially reduce the efficiency of calcium sulphate, since the chloride is rapidly removed. After 177 c. c. of percolate had passed the concentration was only 42 parts per million chlorine in solution and after 333 c. c., no chlorine appeared in the runnings.

For the Fresno soil a comparison of the first six percolates of Table XXI with those of Table XX shows that calcium sulphate has reduced the concentration of the carbonates in the percolates far below that from the natural soil.

Here, too, the calcium sulphate maintained an open structure in the soil favorable to a steady percolation; and the ready access of solution to the soil contributes to the completeness of the conversion of the alkaline carbonates in the soil into the slightly soluble calcium carbonate, with the consequent rapid disappearance of bicarbonate and normal carbonate in the percolate as shown in experiments 3 and 4, Table XXI. In both of these experiments the conversion of normal carbonate to calcium carbonate is seen to be very nearly complete since normal carbonate is practically absent from the leachings, where sodium chloride is added; and it was not found, in the percolate where only calcium sulphate had been added to the soil. To reduce the concentration of the percolate from the natural soil to 40 parts per million bicarbonate, required 1,000 c. c. of water; but on adding calcium sulphate only about one-third of this volume of percolate was needed to reach this same concentration of bicarbonate.

The total quantity of bicarbonate leached by 3,756 c. c. of water from the natural soil was 0.3773 gram. When 672 c. c. of water had been passed throuh the soil treated with calcium sulphate, 0.0984 gram bicarbonate had been removed. Supposing that the concentration in succeeding percolates had remained constant at 40 parts per million bicarbonate, and they undoubtedly averaged much below this figure, the passage of 3,084 c. c. additional water would have carried into solution 0.1234 gram of bicarbonate, making in all 0.2218 gram. This is without doubt much higher than experiment would have shown, but even so is 60 per cent of the quantity which was actually washed from the untreated soil.

TABLE XXII.—*Effect of calcium sulphate upon the removal of black alkali by leaching.*

Soil.	Na_2CO_3 added.	$CaSO_4$ added.	NaCl added.	Carbonate.		
				Maximum CO_3 in solution.	Water required to remove CO_3.	Total CO_3 leached (100 gs. soil).
	Grams.	*Grams.*	*Gram.*	*P. p. m.*	*C. c.*	*Gram.*
North Yakima				223	2,490	0.1404
Do		10		69	30	.002
Do		10	0.75	60	333	.0158
Fresno				81	679	.0103
Do		10		0	0	0
Do		10	.335	15	122	.0016

Soil.	Bicarbonate.				Chlorine.		
	Maximum HCO_3 in solution.	Minimum HCO_3 in solution.	Water required to reduce HCO_3 to minimum.	Total HCO_3 leached (100 gs. soil).	Maximum chlorine in solution.	Water required to remove chlorine.	Total chlorine leached.
	P. p. m.	*P. p. m.*	*C. c.*	*Gram.*	*P. p. m.*	*C. c.*	*Gram.*
North Yakima	4,100	39	4,276	0.7283	193	739	0.02615
Do	656	40	334	.1206			
Do	223	47	426	.0428	6,560	333	.466
Fresno	4,125	33	1,014	.3773	101	216	.0317
Do	1,515	46	296	.0984			
Do	263	45	450	.0326	10,640	173	.7323

The presence of sodium chloride in Yakima black alkali soil causes decrease in the quantity of bicarbonates which must be leached before the percolates reach a concentration below that dangerous to plants. When above 400 c. c. of the liquid had percolated, the solution had reached a fairly steady concentration. At this point over 0.09 gram of bicarbonate has been leached from the soil containing no additional sodium chloride, whereas the same volume of percolate removed about 0.04 gram of bicarbonate from the soil which had been treated with gypsum and sodium chloride. The same phenomenon is met in the case of the Fresno soil. In the case of the Yakima soil the increase in the bicarbonate in the percolates is evidently due to the rapidly decreasing quantity of sodium chloride present. For both soils the final removal of sodium chloride is accompanied by an almost abrupt drop in the concentration of the percolate with respect to bicarbonate.

In conclusion, these experiments indicate that the use of gypsum facilitates the removal of black alkali from soil, although at the same time it adds to the total quantity of alkali present.

ABSORPTION OF POTASSIUM FROM CARBONATE SOLUTION.

The problem of absorption of salts by soils has been studied not only by percolating natural alkali soils with distilled water, determining the quantity of salts removed, but also by the absorption of salt from a percolating salt solution. After introducing into the soil in this manner a considerable quantity of the alkali salt, thus simulating an alkali soil, percolation was commenced with distilled water.

In the following experiments upon the removal and absorption of a base by a soil, a potassium salt was used rather than a sodium salt, on account of the experimental difficulty of determining small quantities of sodium in solution. The normal carbonate of potassium was chosen because previous work gives the form of the curves for the removal of carbonate. The alkaline carbonates, unlike chlorides and phosphates, which were studied by Schreiner and Failyer,[a] have an enormous influence upon the physical condition of the soil.

The experimental difficulty is not so much to regulate the rate of percolation or to keep it sufficiently slow, as to get the solution through the soil at all. One hundred grams of each soil was placed in a paraffined brass tube fitted below with a short section of a Pasteur-Chamberland filter tube, as already described. The solution was percolated through the soil under a head of 6.5 feet water pressure aided by nearly an atmosphere of suction from a filter pump applied below. This pressure was just sufficient for the needs of the experiment.

Four soils, Galveston clay, Marshall silt loam, Hagerstown loam, and Norfolk sand, were percolated with a solution of potassium carbonate containing 444 parts potassium per million parts of solution, and the potassium in the percolates determined colorimetrically[b] for low concentrations and gravimetrically as the chlorplatinate, when the fractions became stronger. The results are given in Tables XXIII to XXVI, and shown graphically in figure 8, which represents the curves of absorption up to the maximum of each, and from that point on the leaching process appears. The data for these leaching curves are contained in Tables XXVII, XXVIII, and XXIX. Each curve in figure 8 gives the total grams of potassium contained by 100 grams of soil—air-dry weight—at each stage of the absorption process.

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[a] Bul. No. 32, Bureau of Soils, U. S. Dept. Agr., 1906; Jour. Phys. Chem., **10**, 239, 361 (1906).

[b] Bul. No. 31, Bureau of Soils, U. S. Dept. Agr., 1906.

The Galveston clay is still absorbing potassium after five months' continuous percolation, during which time 1.13 per cent of potassium has been absorbed by the soil and the concentration of the percolate with respect to potassium has risen to a little over one-third of that for the solution added to the clay, so that we may expect a very considerable quantity of potassium to be absorbed on further percolation. But it seemed inadvisable to prolong the experiment, since the clay had been shown to have a very high absorptive capacity for potassium and would require a very long time for saturation and for subsequent removal of the salts by percolation. Further points on the curve could give, in addition, only the value of the specific absorptive capacity, from a solution of this concentration. This

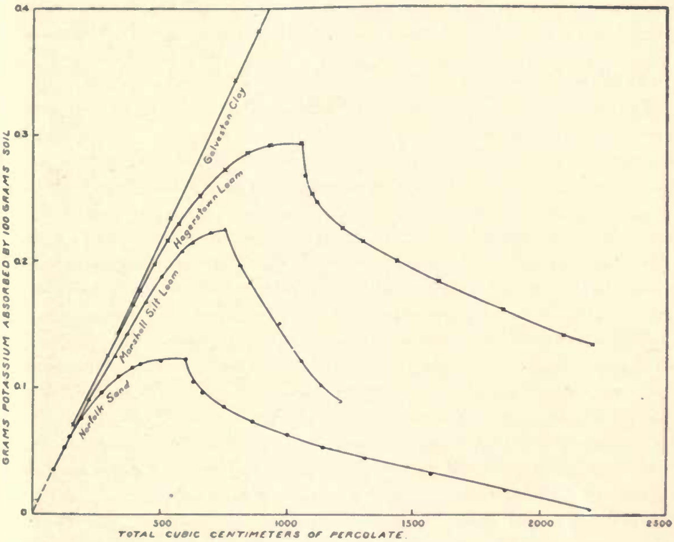

FIG. 8.—Curves showing the total quantity of potassium absorbed from potassium carbonate solution percolating through soils, and the subsequent removal of this absorbed potassium by leaching with distilled water.

absorptive capacity is known for the three other soils used, and the formula $\frac{dy}{dv} = K(A - y)$ proposed by Schreiner and Failyer may be applied.

Table XXIV shows that after some 750 c. c. of the potassium carbonate solution has passed through Marshall silt loam the soil has taken up very nearly all the potassium that it can absorb from a solution of the strength used. Here A, the absorptive capacity of Marshall silt loam for potassium—from this particular concentration of aqueous potassium carbonate—may be taken as 0.230 gram potassium per 100 grams soil. Using this value for A, the results given in Table XXIV conform well to the rate equation of Schreiner and Failyer, $\frac{dy}{dv} = K(A - y)$. For Hagerstown loam, Table XXV, the absorptive capacity, A, is 0.300 gram potassium per 100 grams soil, and the rate of absorption conforms to Schreiner and Failyer's formula, as is also the case for Norfolk sand, whose A, is 0.1226 gram potassium per 100 grams soil, as shown in Table XXVI.

Comparing the soils we see that Hagerstown loam absorbs 0.300 gram, Marshall silt loam 0.230 gram, and Norfolk sand 0.123 gram of potassium per 100 grams of soil. These absorptive capacities are not directly proportional to the areas of the soils per gram as calculated from the mechanical analysis already given.

The absorptive capacity of a soil for potassium from potassium carbonate solution is greater than from potassium chloride solution. Schreiner and Failyer[a] give 1,000 parts per million potassium as the A, for a clay soil in chloride solution containing 200 parts per million potassium; and 650 parts per million as the A for a clay loam under the same conditions. This is a percentage of 0.1 and 0.065, respectively, while Galveston clay absorbed 1.13 per cent, Marshall silt loam 0.23 per cent, Hagerstown loam 0.30 per cent, and Norfolk sand 0.123 per cent potassium—reckoned on the air-dry weight of the soils—from carbonate solution. It is to be remembered that this carbonate solution was more than twice as strong with respect to potassium as the chloride solution used by Schreiner and Failyer. But even taking account of this factor the soils are seen to abstract relatively more potassium from carbonate solution than from chloride solution.

In columns 4 and 5 of the Tables XXIII to XXVI are given the rates of absorption in grams potassium per 100 grams soil per hour, and the rates of percolation in cubic centimeters per hour. The data show a steady decrease in rate of flow as percolation proceeds till a state is reached where the soils seem to form channels and allow the solution to filter faster, and then to close these channels and retard the flow of liquid so that its rate of percolation returns nearly to that prior to the formation of the channels. The initial decrease in rate of flow is not due to packing down of the soils, since they were percolated with distilled water for weeks before any of the potassium carbonate was run through them, but to the puddling or deflocculation produced by the alkaline solution. After the soil is impregnated with alkali the passage of the strong potassium carbonate solution through it is faster than the subsequent flow of distilled water, but as the potassium is washed out the rate increases again.

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[a] Bul. No. 32, Bureau of Soils, U. S. Dept. of Agr., 1906, p. 37; Jour. Phys. Chem., **10**, 361 (1906).

This may be referred to the flocculating and deflocculating action upon the soil grains by the same solute at different concentrations, which has been discussed previously. The production of large floccules would of course permit the solution to pass through more readily and the subsequent breaking down into smaller aggregates would offer a much less permeable percolation bed.

At the beginning of leaching it was necessary to subject the Hagerstown loam to suction under a force of about an atmosphere in addition to the constant head of water, but as leaching proceeded this suction was removed to avoid too rapid percolation. Consequently the rate of percolation for this soil as given in column 5 of Table XXVIII is not exactly comparable with the similar data in Tables XXVII and XXIX. This set of figures on the rate of percolation enables one to compare the rate of absorption with the rate of flow.

The continual decrease in the rate of removal of potassium from these three soils as shown in figure 8, and in the concentration of the percolates given in Tables XXVII, XXVIII, and XXIX, is similar to that for the removal of carbonate, bicarbonate, and chlorine from the natural alkali soils of Yakima and Fresno.

The removal of potassium absorbed by soil from a carbonate solution gives a leaching curve closely resembling that for the removal of potassium absorbed from chloride solution.[a]

The absorption of potassium from carbonate and from chloride solution is likewise described by curves similar in form, and very nearly represented by the formula $\frac{dy}{dv}=K(A-y)$, which also expresses well the rate of absorption and rate of removal of the phosphate radical, PO_4, from soils[a] regardless of what phosphate was used to saturate the soil.

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[a] Bul. No. 32, Bureau of Soils, U. S. Dept. Agr., p. 36.

TABLE XXIII.—*Absorption of potassium from carbonate solution by Galveston clay.*

[100 grams soil. Solution containing 444 parts per million potassium.]

Total percolate.	Potassium in percolate.	Potassium absorbed by 100 grams soil.	Rate of absorption.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Grams.*	*Gram per hour.*	*C. c. per hour.*	*Hours.*
15	13	0.0065	0.00043	1.00	15.0
25	13	.0108	.00062	1.44	21.9
54	13	.0232	.00062	1.45	41.9
90	9	.0388	.00063	1.46	66.7
158	14	.0679	.00066	1.54	110.9
199	14	.0855	.00066	1.54	137.5
228	16	.0978	.00066	1.54	156.2
271	15	.1162	.00067	1.56	183.8
297	14	.1273	.00068	1.57	200.3
335	15	.1435	.00067	1.57	224.5
411	14	.1707	.00067	1.58	272.5
465	15	.1992	.00069	1.57	305.8
545	17	.2332	.00065	1.53	358.1
802	19	.3423	.00054	1.38	445.6
896	24	.3818	.00054	1.29	518.6
993	32	.4217	.00050	1.22	598.1
1,043	34	.4422	.00048	1.17	640.9
1,168	58	.4904	.00048	1.24	741.9
1,248	76	.5198	.00042	1.16	811.2
1,363	63	.5615	.00044	1.21	906.5
1,464	90	.5970	.00037	1.06	1,002.2
1,566	102	.6319	.00035	1.02	1,102.2
1,663	80	.6671	.00038	1.05	1,194.2
1,763	72	.7042	.00039	1.04	1,260.2
1,868	73	.7431	.00031	.84	1,385.2
1,925	175	.7564	.00020	.84	1,453.2
2,033	102	.7933	.00029	.86	1,578.2
2,154	165	.8270	.00023	.83	1,724.2
2,294	186	.8632	.00022	.82	1,896.2
2,429	167	.9005	.00022	.81	2,073.7
2,582	113	.9512	.00026	.80	2,266.7
2,711	152	.9891	.00020	.68	2,458.2
2,860	149	1.0331	.00029	.71	2,670.0
2,949	170	1.0574	.00009	.54	2,835.5
3,043	195	1.0808	.00005	.22	3,268.0
3,105	178	1.0972	.00011	.42	3,415.0
3,213	145	1.1294	.00017	.56	3,607.0

TABLE XXIV.—*Absorption of potassium from carbonate solution by Marshall silt loam.*

[100 grams soil. Solution containing 444 parts per million potassium.]

Total percolate.	Potassium in percolate.	Potassium absorbed by 100 grams soil.	Rate of absorption.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Grams.*	*Gram per hour.*	*C. c. per hour.*	*Hours.*
48	7	0.0210	0.00088	2.00	24
145	24	.0615	.00169	4.00	48
225	83	.0904	.00120	3.33	72
325	94	.1254	.00100	2.85	107
372	95	.1418	.00068	1.96	131
403	97	.1526	.00065	1.86	148
445	98	.1674	.00062	1.77	172
469	100	.1757	.00052	1.53	188
508	135	.1877	.00034	1.29	223
558	189	.2004	.00026	1.04	271
590	244	.2066	.00013	.66	319
630	275	.2140	.00016	.87	365
676	318	.2198	.00008	.64	437
696	350	.2217	.00004	.42	485
732	390	.2237	.000028	.50	557
756	400	.2248	.000023	.50	605

TABLE XXV.—*Absorption of potassium from carbonate solution by Hagerstown loam.*

[100 grams soil. Solution containing 444 parts per million potassium.]

Total percolate.	Potassium in percolate.	Potassium absorbed by 100 grams soil.	Rate of absorption.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Gram.*	*Gram per hour.*	*C. c. per hour.*	*Hours.*
160	6	0.0700	0.00291	6.68	24
292	23	.1245	.00226	5.5	48
392	43	.1648	.00165	4.14	72
478	75	.1966	.00065	1.79	120
530	97	.2146	.00075	2.16	144
573	115	.2287	.00059	1.79	168
630	167	.2445	.00066	2.37	192
657	200	.2513	.00028	1.14	216
696	215	.2602	.00039	1.62	240
753	240	.2718	.00024	1.19	288
796	275	.2790	.00016	.90	336
845	301	.2857	.00015	1.09	380
902	360	.2907	.00007	.80	452
934	406	.2919	.000025	.67	500
983	424	.2929	.000014	.67	572
1,016	428	.2934	.000011	.69	620

TABLE XXVI.—*Absorption of potassium from carbonate solution by Norfolk sand.*

[100 grams soil. Solution containing 444 parts per million potassium.]

Total percolate.	Potassium in percolate.	Potassium absorbed by 100 grams soil.	Rate of absorption.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Grams.*	*Gram per hour.*	*C. c. per hour.*	*Hours.*
82	5	0.0360	0.00015	3.39	24
122	37	.0523	.000068	1.69	48
193	107	.0762	.0000996	2.96	72
274	193	.0966	.0000425	1.69	120
313	232	.1048	.0000344	1.62	144
338	261	.1098	.0000191	1.04	168
370	305	.1142	.0000183	1.34	192
389	330	.1164	.0000092	.79	216
420	365	.1189	.0000052	1.29	240
464	407	.1205	.0000033	.92	288
502	417	.1216	.0000023	.78	336
546	422	.1226	.0000021	.92	884
600	444	.1226	....	.76	442

TABLE XXVII.—*Leaching of potassium from Marshall silt loam.*

[100 grams, containing 0.2248 gram potassium, absorbed from K_2CO_3 solution.]

Total percolate.	Potassium in percolate.	Potassium left in soil.	Rate of leaching.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Gram.*	*Gram per hour.*	*C. c. per hour.*	*Hours.*
0	0	0.2248	....	....	0
17	471	.2168	0.000187	0.354	48
36	513	.2070	.000168	.346	103
59	426	.1972	.000123	.290	183
72	410	.1919	.000125	.304	226
95	375	.1833	.000086	.228	327
125	273	.1751	.000050	.183	492
162	151	.1695	.000053	.386	588
194	273	.1607	.000088	.320	688
217	320	.1533	.000039	.123	876
235	350	.1470	.000033	.094	1,069
256	412	.1383	.000033	.080	1,333
301	278	.1258	.000035	.125	1,693
336	337	.1140	.000030	.091	2,078
369	230	.1064	.000020	.088	2,456
390	190	.1024	.000009	.044	2,889
412	202	.0979	.000031	.150	3,036
435	162	.0942	.000019	.120	3,228
456	166	.0907	.0000185	.111	3,417

TABLE XXVIII.—*Leaching of potassium from Hagerstown loam.*

[100 grams, containing 0.2934 gram potassium absorbed from K_2CO_3 solution.]

Total percolate.	Potassium in percolate.	Potassium left in soil.	Rate of leaching.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Gram.*	*Gram per hour.*	*C. c. per hour.*	*Hours.*
0	0	0.2934			
24	538	.2805	0.00026	0.50	48
51	490	.2673	.00024	.49	103
85	436	.2525	.000107	.43	183
103	311	.2469	.000131	.42	225
144	237	.2376	.000092	.40	326
169	256	.2312	.000093	.36	395
206	145	.2258	.000056	.39	490
243	151	.2202	.000058	.39	586
280	133	.2153	.000044	.37	686
311	90	.2124	.000030	.34	772
346	107	.2087	.000039	.37	868
393	116	.2032	.000047	.38	994
416	114	.2006	.000039	.34	1,062
460	114	.1956	.000040	.35	1,187
511	100	.1905	.000035	.35	1,333
581	90	.1842	.000033	.36	1,525
637	82	.1796	.000027	.34	1,692
704	82	.1741	.000029	.35	1,885
774	87	.1680	.000032	.37	2,077
841	82	.1625	.000026	.32	2,289
896	76	.1583	.000025	.33	2,455
1,032	83	.1470	.000026	.32	2,887
1,077	89	.1430	.000027	.31	3,034
1,136	75	.1386	.000023	.31	3,226
1,191	82	.1341	.000024	.29	3,415

TABLE XXIX.—*Leaching of potassium from Norfolk sand.*

[100 grams, containing 0.1226 gram potassium absorbed from K_2CO_3 solution.]

Total percolate.	Potassium in percolate.	Potassium left in soil.	Rate of leaching.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Gram.*	*Gram per hour.*	*C. c. per hour*	*Hours.*
0	0	0.1226			
30	582	.1051	0.000314	0.63	48
67	236	.0964	.000159	.67	103
119	138	.0892	.000091	.66	183
148	125	.0856	.000085	.68	226
219	105	.0781	.000074	.70	327
265	97	.0736	.000070	.67	396
335	71	.0686	.000053	.74	491
403	83	.0630	.000059	.71	587
476	75	.0575	.000055	.73	687
541	63	.0534	.000044	.71	779
616	59	.0490	.000046	.78	875
708	53	.0441	.000039	.74	1,000
759	49	.0416	.000037	.75	1,068
857	48	.0369	.000038	.75	1,193
967	42	.0323	.000032	.92	1,339
1,124	44	.0254	.000040	.81	1,510
1,259	41	.0199	.000041	.80	1,678
1,422	43	.0129	.000043	.85	1,871
1,592	44	.0044	.000039	.89	2,063
1,742	34	− .0007	.000024	.71	2,275
1,897	25	− .0046	.0000236	.94	2,330
2,142	21	− .0083	.000019	.57	2,763
2,322	18	− .0116	.000022	1.22	2,910
2,512	4	− .0124	.000004	.99	3,102
2,707	2	− .0128	.0000019	1.08	3,291

Thus we have shown that the removal curves for bicarbonate, carbonate, chlorine, potassium, and phosphate leached from soils are very similar in form.

It has also been demonstrated by these percolation studies that the absorptive capacity of soils is very considerable, large quantities of both acid and basic radicals being retained. These are again released by the soil to fresh additions of water and to the soil solution, as the plants remove the nutrient salts.

SUMMARY.

In the foregoing pages the work on absorption by soils, which has been in progress in the Bureau for some years, has been continued and a further and more complete study has been made of the composition of the solutions and the quantity of material removed from solution by the soil. The literature upon the subject of absorption has been brought together.

In the experiments described the materials used are not always fertilizer salts or constituents of the soil itself, since other substances, particularly certain dyestuffs, are better adapted to obtaining a more detailed knowledge of the mechanism of absorption. In general, it may now be stated that where disturbing influences are not great the mathematical formulation may be made both of the time rate and of the absorption and distribution of the material between the solid and the liquid. The disturbing influences, however, are quite important in most cases actually met in practice, and therefore a detailed study of some of them was undertaken. The most important of these is the change in the physical character of the soil itself, consequent upon the absorption of the dissolved materials. In some cases, notably with acids and with lime, the soils assume a "flocculated" structure, i. e., a great many of the ultimate grains form larger aggregates or "ball together;" and in other cases, especially with alkalies, the soils are deflocculated, each grain standing out separate and distinct from the others. This change in the structure of the soil is of the utmost importance in influencing the physical condition of the soil, which in turn influences the drainage condition, the aeration of the soil, its capacity to hold he soil solution and control its movement through the soil, the composition of the soil solution, the character and rate of the chemical changes taking place in the soil solution; and, in fact, in influencing directly both the physical and chemical factors which are the most important in governing the proper growth of plants.

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BUREAU OF SOILS—BULLETIN No. 53.

MILTON WHITNEY, Chief.

THE ISOLATION OF HARMFUL ORGANIC SUBSTANCES FROM SOILS.

BY

OSWALD SCHREINER AND EDMUND C. SHOREY.

WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1909.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., May 14, 1908.

Sir: I have the honor to transmit herewith the manuscript of a technical paper entitled, The Isolation of Harmful Organic Substances from Soils, by Oswald Schreiner and Edmund C. Shorey, of this Bureau. This article is the result of a study of several unproductive soils, and deals with the properties of crystalline bodies isolated therefrom.

The material throws considerable additional light upon the question of soil fertility. The manuscript has been gone over carefully with Assistant Secretary Hays, who concurs in my recommendation for its publication as Bulletin No. 53 of the Bureau of Soils.

Respectfully,

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

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THE ISOLATION OF HARMFUL ORGANIC SUBSTANCES FROM SOILS.

THE PRESENCE OF HARMFUL SUBSTANCES.

Investigations into the causes of the infertility of soils have established three facts which may be considered fundamental in any discussion of the subject. These are: First, soils may be infertile because of the presence in them of some substance or substances inimical to plant growth. Second, many plants produce and possibly excrete, as the result of growth, organic compounds which are poisonous to the plants producing them. Third, many of the organic constituents of plants which on the death and decay of vegetation find their way into the soil, or compounds which may arise during subsequent changes in the soil, inhibit growth when presented in solution to the roots of growing plants.

The facts on which these three generalizations are based have been published in detail[a] and will be but briefly presented here.

The essential facts regarding the first proposition are these: Aqueous extracts of soil retain the fertile or infertile properties of the soils from which they are made. A water extract of a poor soil is a poorer medium for the growth of plants than an extract of a good soil. The growth of seedlings in an extract of an infertile soil is often less than in pure distilled water. Since, however, the distilled water contains no mineral nutrients whatever, while the poor soil extract contains some, the diminished growth in the latter must be due to the presence of something harmful, something that hinders the plant's development, even in the presence of the nutrients in the soil solution and those stored in the seed. This simple experiment is sufficient to establish this, but there are a number of other observations thoroughly in accord with the conclusion stated. Dilution of a poor soil extract often makes it a better medium for the growth of seedlings than the original extract. Treatment of such an extract with some absorbing agent, such as carbon black or ferric hydrate, which furnishes no mineral plant food, has the same effect. In other words, any treatment which dilutes the inhibitory material in the soil extract makes it better even when the mineral plant food is diminished at the same time. In further accord with these observations is the fact that the addition of certain chemicals which furnish no plant food often improves poor soil extracts. Pyrogallol is such a compound, the improvement being evidently due to some change in the harmful material brought about by the added compound, or else it enables the plant to overcome the harmful effect.

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[a] Buls. Nos. 23, 28, 36, 40, 47, Bureau of Soils, U. S. Dept. Agr.

The second proposition, viz, that roots may excrete harmful bodies, is based, first, on the behavior of the roots of wheat seedlings when grown in agar-agar in which wheat had been previously grown,[a] and, further, on the fact that from soils in which wheat and cowpeas had been grown until the growth was greatly diminished crystalline substances have been obtained which were found to be inhibitory to wheat and cowpeas, respectively, when these were grown in water solutions of these substances.[b] These substances could not be obtained from these soils before the repeated growth of wheat and cowpeas.

The third proposition has to do with the constituents of plants that on the death and decay of vegetation become part of the soil, in contradistinction to those which may possibly be excreted during the growth of the plant. The number of such compounds which have been studied with respect to their toxicity to plants when compared with the number which may possibly find their way into the soil is very small, and no sweeping conclusions can be drawn as to what classes of compounds are and what are not inhibitory to plant growth. The work done, however,[c] is sufficient to establish the fact that many such constituents are harmful. In view of the great number of such compounds, this work might be continued almost indefinitely, but since many of these plant constituents are undoubtedly soon changed into other compounds in the decay which dead vegetation undergoes in the soil, such continuation does not seem to be the best way in which to attain the end which is the object of fertility studies, viz, profitable rotation and rational fertilization. Once it has been established that some plant constituents are harmful, the attainment of this end seems to lie in the study of such bodies as are actually in the soil under infertile conditions and the way in which they arise in the soil.

To the three general statements made above there may be added, as a supplementary proposition, that the harmful compounds in soils which render them infertile or "exhausted" are organic compounds. There are, of course, soils which are infertile owing to the presence of excess of mineral salts, such as common salt, alkaline carbonates or sulphates, ferrous compounds, etc., but where such is the case the cause is generally easily discernible. With conditions such as these the present studies do not deal. By inhibitory or harmful soil compounds is here meant that residue of the complicated processes of plant life and plant decay which becomes an integral part of the soil; which causes the yield, when the same crop is grown continuously on some soils, to become less and less; which often renders the application of fertilizers necessary in the presence of a sufficiency of mineral plant food; which often compels the abandonment of the crop best suited to climate or market, or else forces a rotation with a less remunerative crop; which prevents the chemist diagnosing the cause of soil infertility by any of the numerous methods of analysis in use; which has rendered of no avail many elaborately planned plat experiments; and which is the cause of a natural succession of wild vegetation not explained by any change of soil or climate.

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[a] Bul. No. 40, Bureau of Soils, U. S. Dept. Agr.

[b] Schreiner and Sullivan, Science, **27**, 329 (1908).

[c] Bul. No. 47, Bureau of Soils, U. S. Dept. Agr.

The evidence that the inhibitory bodies which cause infertility are organic compounds is both direct and indirect. As indirect evidence we have the absence of harmful inorganic material; the ready changes in many cases from harmful to nonharmful form by oxidation, whether by the roots of growing plants or by cultivation; the similar change effected by the addition of chemicals, both fertilizer salts and others; the change in injurious properties in many cases on heating, and in other cases the carrying over of the harmful properties on distillation, or removal by burning. Finally, the fact that the roots of growing plants possibly excrete harmful material which behaves as organic matter, and the fact that many organic plant constituents which find their way into the soil are inhibitory to plants, make the conclusion as certain as one based on indirect evidence can be. As final proof that there are in soils organic bodies harmful to plants, there is, as will be shown in the sequel, the isolation and identification of organic bodies from the soil which are inhibitory to plant growth, and which behave in solution as does the extract from an infertile soil.

The end sought in this study of soil fertility is a better understanding of the causes of infertility, and through this the removal, amelioration, or prevention of those bad soil conditions that may be the proximate causes of infertility, even when the real causes are the compounds formed under such conditions.

STATEMENT OF PROBLEM.

The extension of the investigation beyond the generalizations mentioned above involves, among others, three problems, each complex in itself. These are the identity and nature of the harmful substances in soils, their sources or the way in which they get into the soil, and finally the relation of harmful substances to each other, to nontoxic or even beneficial substances, and to added bodies such as fertilizers, both organic and inorganic.

These problems, especially the last stated, are very complex, and it would seem most improbable that the practice of agriculture could ever become scientific, except through the complete clearing up of the questions involved. Every effort should be made, then, to shed light on the identity, source, and general properties, including destruction or alteration, of inhibitory compounds. It is only by this that the practice of agriculture can be placed on the same plane with other great industries which have profited so much by scientific research in the past, a scientific development in which agriculture has not shared to its fullest extent.

With the first of the problems stated, the isolation, identification, and general properties of harmful soil compounds, the present paper is chiefly concerned.

The questions which naturally arise on a first approach to this problem are, first, what is the origin of the organic matter in general in the soil, what kind of substances furnish the material out of which the organic portion of soils is made, and what changes or transformation does it undergo in the soil? Second, are any of the organic compounds which first inquiry may have shown to become part of the soil, or to be formed in the soil, harmful to plants in the small amounts in which they would probably be present?

If in pursuit of this second inquiry it is found that some of the substances which get into the soil, or others which we must conclude are formed in the soil, are harmful, a further question arises. Have any of these substances been found in soils, or may there not be in the soil other substances which, because of insufficient data, have not been considered at all up to this point? The possibility of the presence in soils of compounds, of which neither the presence nor effect could be predicted, or even suspected, at once makes the inquiry the more general one, what do we know of the organic matter in the soil? The problem of the isolation, identification, and study of the general properties of organic soil compounds is, as has been stated, a complex one not only in itself but in its relations to other problems in soil fertility.

SOURCES OF THE ORGANIC MATTER OF SOILS.

An essential difference between soil and a mere mass of sand or disintegrated rock is that the former contains some organic matter. The first step in the transformation of bare rock into soil must be accomplished by the lowest forms of plant life, which obtain the materials necessary for their growth and reproduction from the air, rain water, and mineral matter dissolved from the rock. The death of these furnishes organic matter which can be utilized by higher forms, and thus the process goes on until there is an accumulation of organic matter sufficient, with the disintegrated rock material, to be called an arable soil and furnish a medium suitable for the growth of higher plants and agricultural crops. When the process of soil formation has reached this stage the number of micro-organisms, which at first were probably confined to a few species, is greatly increased, including bacteria and fungi of widely varying habits of growth and varied products resulting from this growth. There is, then, entering into the organic matter of a soil on which wild plants or crops are growing the remains of such parts of these plants as die and any products from the living plants. Still other compounds result from these through the growth of micro-organisms, by the oxidizing action of plant roots, by cultivation or lack of it, and by changes effected by fertilizers. Finally there are remains of micro-organisms themselves. It is probable that animal remains, such as insects and worms, should be accorded a more prominent place as a source of soil organic matter than is usually given them, for the amount of such material returned to the earth is very large. Earthworms are also an important factor, for they not only furnish animal remains, but much of the organic matter of plant origin is changed by passage through their digestive tract.

The final result of these complicated processes, it is hardly necessary to say, must be a mixture fully as complex as the processes through which it arises, and even when the original material has been similar in character the organic residue may be very different under varying conditions of temperature, moisture, aeration, cropping, and the character of micro-organisms present.

It is usual to consider the organic matter of both plants and animals as made up of protein, fats, and carbohydrates, but in addition to these elements there are, particularly in plants, a host of other compounds not included in these groups and which are a source of no small part of the soil organic matter. Among these are resins, hydrocarbons and derivatives, waxes, alkaloids, glucosides, tannins, phenols and their derivatives, acids, aldehydes, etc.

When the complex molecules of proteins, fats, and carbohydrates break down into simpler bodies they split along the same lines of cleavage, depending on the structure of the original molecule, be it through the agency of micro-organisms as in decay, the agency of enzymes in digestion or agents such as acids or alkalies in the laboratory. These simpler bodies, which are termed primary cleavage or degradation products, are no doubt formed in the soil as elsewhere as the first steps of decay.

These primary cleavage products, however, particularly in the case of protein, are subject to still further decomposition through the same or other agencies. These secondary products are very numerous and of widely varying composition, structure, and, of course, chemical and physiological properties. To this is due the very different final products of decay or putrefaction under different conditions. To this variation in secondary decomposition products under different conditions of temperature, moisture, aeration, etc., the varying character of the organic matter in soils is probably due more than to differences in the plant or animal material which originally goes into the soil.

The number of such secondary products that may be formed is very large, and includes gaseous products which are the final stages of the decomposition of the organic matter into its elements, and practically all intermediate compounds between the original complex molecules and the final simple compounds. In other words, there is a continual "building down" process from the original complex molecule to simpler ones and these again into still simpler molecules, and so on down to the elemental stages of matter.

In addition to these various decomposition products in the soil, there are compounds which are built up by micro-organisms from the simpler degradation products. This reversal of the decomposition of the original organic matter into simpler compounds, by synthetic processes effected by micro-organisms, or possibly other agents, adds materially to the complexity of the problem.

Among the unclassified organic compounds spoken of above, such as resins, terpenes, tannins, etc., are some which are very resistant to decomposition by the agents active in the soil, and these may often exist in the soil in their original condition, at least for a time. On the other hand a great many break down into simpler bodies, as do the proteins and carbohydrates.

We have, then, as possible organic compounds in the soil, all plant constituents, compounds of animal origin, their degradation products, both primary and secondary, and also other products built up from these. Any attempt at complete enumeration of these would simply result in a long list of organic compounds with almost every class of such compounds known to science represented, and mention will be made here of but a few of the more prominent ones. Proteins, which are present in all parts of living plants, are complex compounds the constitution of which has not yet been established. These in decay, as has already been stated, break down into simpler bodies, most of which have been thoroughly studied and their composition and constitution well established. Among these simpler bodies, which are nearly all nitrogenous, may be mentioned glycocoll, asparagine, alanine, leucine, phenylalanine, tyrosine, arginine, histidine, and lysine. Fatty acids may be present in plants either as free acids, in combination with glycerol as glycerides, or as part of the more complex molecule of lecithins. Stearic and oleic acids are present in some of these forms in nearly all plants, and there are in addition to these a large number of other fatty acids the distribution of which is in many cases limited to a few related species of plants. The composition and constitution of these is known in most cases, but with the exception of lecithins these fatty bodies are not so readily subject to breaking down in decay as are the proteins, and there is much less known of the products of such breaking down. The lecithins in breaking down give rise also to another class of bodies—choline, neurine, and betaine—all being well-known definite organic compounds of a basic nature.

The numerous substances formed during plant growth which are generally regarded as nonessential in the economy of the plant furnish a large amount of soil organic matter and include a large number of well-defined organic compounds. Among these are the alkaloids, terpenes, phenols, vegetable acids, and derivatives of these bodies. The composition and constitution of many alkaloids is well established; a large number being pyridine or quinoline derivatives, readily break down into simpler bodies like the pyridine or quinoline carboxylic acids, themselves well-defined compounds. The terpenes constitute another class of this kind, being widely distributed and including a large number of compounds, the composition and constitution of which is well known. Pyrocatechol, vanillin, cumarin, coniferin, and vegetable acids such as oxalic, citric, tartaric may be cited as examples of other well-known plant constituents.

It is evident from this brief survey of this phase of the problem that although the organic matter which goes into the soil is of an exceedingly varied and complex character, and that which forms in the soil may be even more so, there is considerable definite information available regarding the character of some of it. A great number of plant constituents, as well as the bodies to which they give rise on decay, are well-known definite chemical compounds. Some of these substances it requires no argument to prove get into the soil on the death of the plants containing them; others may be assumed to be formed in the soil. The question now arises, are any of these harmful to plants in the comparatively small quantity in which we might expect them to be present in soils?

EFFECT OF CERTAIN ORGANIC COMPOUNDS ON PLANTS.

There is in the literature considerable information regarding the injurious effects of various organic compounds on fungi, bacteria, algæ, and some of the higher plants, but for the most part these investigations have been purely physiological and have had no reference to, or direct bearing on, agricultural crops or soil studies. Either the compounds tested have no soil interest, the plants were lower forms, or the measure of inhibition or injury was based on some special function of the plant and not the general one of plant development.

It is not difficult to account for the dearth of data on the injury from organic soil compounds. The prominence given the mineral plant food theory of Liebig and the exclusion of almost every other consideration in dealing with the unproductiveness of soil brought about such a condition that from Liebig's time to the present the idea that organic compounds inhibitory to plant growth might be factors in the infertility or exhaustion of soil had practically no place in the philosophy of agricultural chemists.

Practically all that is known regarding the harmful effect of the organic compounds which get into the soil, or may arise in the soil, has been presented in another bulletin.[a] The most important point—at least in this connection—established by the investigations there reported is that many of the possible organic soil compounds are harmful to plants, some in very small amounts.

From these investigations no general conclusions regarding the connection between effect on plants and chemical constitution were drawn, nor are the data sufficient to form the basis of any complete classification of such bodies. However, the establishing of a relation between effect and chemical constitution was not the object of these investigations, but rather to determine whether some plant constituents which get into the soil or compounds which may arise from them in the soil, are harmful to plants, in small amounts. This has been abundantly proven. It is also a matter of everyday observation that material containing many of the compounds found harmful is constantly being added to the soil. Many of the protein decomposition products, such as asparagine and leucine, not only are not harmful but appear to act as plant nutrients; others again, such as tyrosine, are injurious in quite small amounts. Choline was found to be harmful only in relatively high concentration, while the closely related neurine was injurious in concentrations very much less, and betaine, also closely related to both, was innocuous. The most markedly harmful bodies were found among those deposited within the plant but apparently not a part of the life of the plant. Arbutin, vanillin, cumarin, heliotropine, esculin, terpenes, all of which are found to be very injurious, belong to this class.

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[a] Bul. No. 47, Bureau of Soils, U. S. Dept. of Agr.

Although there may be many plant constituents which are harmful to plants, and although it is evident that many such plant constituents must get into the soil on the death of vegetation, it would seem probable that some of them would be soon changed or destroyed by agents active in the soil so that they could not properly be considered part of the soil nor as factors in soil fertility. Others, however, might persist, since they are likewise strongly poisonous to lower forms of life and not readily oxidized for a longer or shorter period of time under certain soil conditions. This brings up another inquiry. Have any of these plant constituents or known derivatives, which are injurious and which are known to get into the soil, actually been separated from the soil? May there not be in the soil harmful organic compounds, the presence of which is not suspected or can not be predicted? These two questions involve a discussion of our knowledge of soil organic matter, first regarding the presence or absence of known compounds and second as to the possible presence of other compounds which could not have been suggested by the knowledge of the origin of soil organic matter.

PREVIOUS ATTEMPTS TO ISOLATE ORGANIC SOIL COMPOUNDS.

The first part of this inquiry can be very shortly disposed of. There is no record in the literature of any of these plant constituents that must get into the soil, or of any compounds that might be expected to be formed from them in the soil, ever having been isolated from any soil. This can not, however, be taken as evidence that these may not be present, for there is also no record that any individual members of this class have been especially or consistently sought for. There are, moreover, as will be shown in subsequent pages, such difficulties involved in this search that in many cases failure to find, by methods commonly used, would not be proof of their absence. The second phase of this question necessarily involves a somewhat full survey of the literature bearing on the subject and an examination of the claims to recognition of compounds described and named in the literature. This survey will serve as a guide in a systematic search for such soil compounds as are harmful to plants and, moreover, is essential to a thorough understanding of the complexity of the problem in hand and its relation to other problems, and furnishes a basis for attacking this complex problem with a reasonable hope of solving some of the intricate questions of soil fertility.

SEPARATION OF SO-CALLED HUMUS BODIES.

Probably the majority of agronomists, soil chemists, and students of soil fertility in general associate soil organic matter with the term "humus" and with humus only. With some there is the assumption that, when speaking of a soil, humus and organic matter are synonymous, and that any organic matter in the soil not humus is simply the undecomposed remains of plants and animals which have not yet reached the stage of decomposition where they can be properly considered a part of the soil. With others there is the assumption that, although there may be organic matter in the soil not humus, it is of such composition or form that it plays no part in the fertility of the soil, having a purely physical effect. Neither of these assumptions is warranted, as will be shown.

The term "humus," as originally used, had no especial agricultural or scientific significance, being simply another name for dark-colored vegetable mold and later applied to this mold material as a constituent more or less of all soils.

The term has now a more restricted meaning, especially as used by agricultural chemists, being applied more exclusively to the dark-colored organic matter extracted from soils by dilute solutions of sodium or ammonium hydrate and often called "humic acid." It is generally conceded, even by those prone to regard humic acid and allied acids as definite organic bodies, that the organic extract so obtained is a complex mixture and the method of determining humus in use to-day, which is essentially that of Grandeau,[a] is merely an empirical method of determining a portion of the organic matter in the soil. Klaproth [b] or Thomson [c] applied the name "ulmin" to dark-colored amorphous bodies such as those obtained by Vauqulin [d] from the bark of diseased elm trees. Sprengel,[e] who obtained similar bodies from soils applied to these the name "humic acid." In 1838 Berzelius,[f] evidently with the general meaning of the term "humus" in mind, used the term "humin" in describing certain dark-colored constituents of vegetable mold. Following this use of the term "humin," as applied to what was considered to be a definite organic body, a number of other workers took up the study of similar bodies and a number of other terms more or less related soon appeared. This group of workers included

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[a] Traité d'analyses des matières agricoles, p. 148, Paris, 1877. Bul. No. 107, Bureau of Chemistry, U. S. Dept. Agr., p. 19.

[b] De Candolle, Pflanzen-Physiologie, I, 279 (1833).

[c] Jour. prakt. Chem., **21,** 325 (1840).

[d] Ann. Chim., **21,** 39 (1797).

[e] Bul. Soc. Chim., **10,** 173; De Candolle, Pflanzen-Physiologie, I, 280 (1833).

[f] Poggendorff's Ann., **44,** 375 (1838).

Braconnot,[a] Mitscherlich,[b] Boullay,[c] Malaguti,[d] and Mulder.[e] The terms applied to humuslike bodies which have appeared more or less in the literature from that time to the present are associated for the most part with Mulder's name. Mulder had very definite ideas regarding the chemical individuality of these bodies. For instance, he says: [f]

> At present seven different organic substances are known to exist in the soil. They are crenic acid, apocrenic acid, geic acid, humic acid and humin, ulmic acid and ulmin.

These bodies he divided into two groups, one group consisting of crenic and apocrenic acids, the other group embracing all the others. As has been said, many of these terms, particularly humic acid, have come down through the literature of agricultural chemistry to the present and are now used with some writers at least with the same faith with which Mulder used them. According to Mulder these seven organic bodies found in soils were intimately related,[g] and five at least were five distinct steps in the decay of organic matter in the soil. He regarded ulmic acid as the first step in this decay; this on further oxidation yielded humic acid and this in its turn, on still further oxidation, geic acid. Continued oxidation produced apocrenic and finally crenic acid. He ascribed to these the following formulas:[h] Ulmic acid, $C_{40}H_{14}O_{12}$; humic acid, $C_{40}H_{12}O_{12}$; geic acid, $C_{40}H_{12}O_{14}$; apocrenic acid, $C_{48}H_{12}O_{24}$; and crenic acid, $C_{24}H_{12}O_{16}$.[i]

All this reads as though the matter were very simple, but the truth is that, although Mulder may have been in many ways in advance of his time, he was not able at a time when organic chemistry was in its infancy to clear up in so simple a manner one of the most complicated problems this branch of science has to deal with, viz, the composition of the organic matter in the soil.

Early investigators, including Mulder, soon found that sugar, starch, carbohydrates generally, and even albuminous bodies, when treated with strong acids or alkalies gave rise to dark-colored compounds having the same general appearance and properties as the humus bodies arising in the soil through decay. The same names were applied to these compounds and there was a general assumption that those in the soil and those produced in the laboratory were the same. As the number of investigators increased there soon arose disagreements regarding the composition of some of these, particularly humic acid, from several sources, it being found that the carbon content of these different preparations varied quite widely. Mulder attempted to reconcile such conflicting figures by showing that there were several kinds of humus and humic acids different in their character and fixed in their composition.[a]

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[a] Ann. Chim. Phys., **12**, 191 (1819).

[b] Lehrbuch, 3rd edit., I, p. 534.

[c] Ann. Chim. Phys., **43**, 273 (1830).

[d] Ann. Chim. Phys., **59**, 407 (1835).

[e] Jour. prakt. Chem., **21**, 203, 321 (1840); **32**, 321 (1844).

[f] The Chemistry of Vegetable and Animal Physiology, trans. by Fromberg, 1849, p. 146.

[g] Loc. cit., p. 150.

[h] Loc. cit., pp. 150 and 162.

[i] These formulas are on the old basis and to be modernized the hydrogen should be doubled.

He held that the different humic acids might have a different composition due to the presence of one or more molecules of water so held that it could not be driven off at 140° C. For instance, he gives the following formulas:[b]

Humic acid from sugar: $C_{40}H_{12}O_{12}$.
Humic acid from hard turf: $C_{40}H_{12}O_{12}+3HO$.
Humic acid from an arable soil: $C_{40}H_{12}O_{12}+4HO$.

One of the points of issue between these early investigators was whether humic acid and allied bodies contained nitrogen as a component. Mulder held that nitrogen was not a component of these bodies but was present as ammonia, that is, the acids were present in the soil as ammonium salts,[c] and in this connection he says:

> In a good arable soil—that is, one in which the organic constituents are as far as possible decomposed—none of these substances contain nitrogen as a constituent element; all their nitrogen exists in the state of ammonia.

Detmer came to the opposite conclusion[d] on this point, claiming that the nitrogen in humic acid as obtained was present in organic combination. His conclusion was based on the fact that his humic acid, containing nitrogen, when treated with potassium hydrate gave off no ammonia, and only a small amount of nitrogen was given off in treatment with alkaline hypobromate. Later, however, Detmer stated that humic acid could be purified and obtained nitrogen free.[e]

He gave for the acid the formula $C_{60}H_{54}O_{27}$ and also gave the following formulas for salts: $C_{60}H_{46}O_{27}Ca_3(NH_4)_2$, $C_{60}H_{46}O_{27}Fe_2(NH_4)_2$, $C_{60}H_{46}O_{27}Ag_8$.

From time to time there have been reported since the preliminary work outlined above, descriptions and formulas for humic acid and related bodies, the net result being about as many formulas as investigators, the only agreement being a general one of source, preparation, and somewhat vague properties.

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[a] Bul. Sc. Phy. et Nat. Neerl., 1840, pp. 1-102.

[b] The Chemistry of Vegetable and Animal Physiology, p. 154. Formulas on the old basis of O=8.

[c] Loc. cit., p. 146. Chemie der Ackerkrume, II, 256 (1862).

[d] Landw. Vers.-Stat., **14**, 248 (1871).

[e] Jahresb. Fortsch. Chemie, 1873, p. 844.

Ulmic acid, according to Malaguti[a] had the formula $C_{12}H_{12}O_6$. Stein[b] ascribed to the humuslike bodies obtained by the action of hydrochloric acid on sugar the formula $C_{24}H_{18}O_9$. Lefort[c] obtained from rotten wood a humic acid to which he ascribed the formula $C_{24}H_{15}O_{17}$. Liebmann and Lettmayer[d] obtained what they claimed was the ammonium sodium potassium salt of humic acid. The humic acid prepared from this by precipitation contained carbon, 53.6 per cent, and hydrogen, 4.9 per cent. Thenard[e] prepared what he claimed was pure humic acid free from nitrogen and ash and gave the formula $C_{24}H_{10}O_{10}$. Mayer[f] obtained from Dopplerite a humic acid having the formula $C_{17}H_{18}O_8$. Demel[g] described the calcium salt of a humic acid having the formula $C_{24}H_{22}CaO_{12}$. Conrad and Guthzeit[h] obtained by action of acids on carbohydrates a humic acid containing 62.3 to 66.5 per cent carbon and 3.7 to 4.6 per cent hydrogen. Hoppe-Seyler[i] described humic acid obtained from brown coal which had the formula $C_{26}H_{22}O_{10}$; but as the barium salt showed the composition $BaC_{26}H_{22}O_{11}$ he considered the body obtained as the anhydride of an acid $C_{26}H_{24}O_{11}$. Berthelot and Andre[j] by the action of hydrochloric acid on sugar obtained a humic acid to which they gave the formula $C_{18}H_{16}O_7$. This, they claim, when heated to 110° C. gave an anhydride $C_{18}H_{14}O_6$. They further described the properties of this body[k] and stated that it was of the nature of a lactone.

As has already been stated, the object in reviewing the literature on this soil organic matter is for the purpose of arriving at some conclusion regarding the availability of such information as may be found there as a guide in a systematic search for such soil compounds as are harmful to plants. In other words, the chief concern at this stage of the present inquiry is the names and composition of humus bodies as definite organic compounds and their claim to recognition as such, rather than the broader question of the source and method of formation of such bodies and their relation to other bodies in the soil.

Leaving discussion of the results obtained by the workers quoted for subsequent pages, it is not out of place here to note that the most conspicuous feature of this work is the discordant results obtained for bodies bearing the same name and often from the same source.

During the period when the early work on humus bodies was being carried on, there was begun an investigation along another closely related line, although at first sight this close relation might not be apparent. This was the study of the coloring matter in urine, either under normal or pathological conditions, or produced by chemical treatment.

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[a] Ann. Chim. Phys., **59**, 407 (1835).

[b] Ann. Chem., **30**, 84 (1839).

[c] Zeitsch. Chem., 1867, p. 669.

[d] Ber. chem. Ges., **7**, 408 (1874).

[e] Jahresb. Fortsch. Chem., 1876, p. 878.

[f] Landw. Vers.-Stat., **29**, 313 (1883).

[g] Monatsh. Chem., **3**, 763 (1883).

[h] Ber. chem. Ges., **19**, 2850 (1886).

[i] Zeitsch. physiol. Chem., **13**, 109 (1889).

[j] Ann. Chim. Phys., **25**, 364 (1892).

[k] Compt. rend., **141**, 433 (1905).

The early work on this subject was, as might be expected, rather crude, and each investigator obtained different results and gave different and sometimes somewhat fanciful names to what they regarded as definite compounds. Udránszky in 1887 gathered together the loose ends left by these investigators and as a result of his own work stated that the darkening of urine on boiling with acids was due to a humuslike body formed from the reducing substances in the urine.[a] Following this came the work of Hoppe-Seyler[b] and Schmiedeberg[c] along closely related lines and it soon came to be recognized by physiological chemists that plant or animal tissues or fluids, if they contain a carbohydrate group, either free or as part of a more complex molecule, will, if heated with strong acids, give rise to bodies of a humus nature. Schmiedeberg drew attention to the fact that the humus bodies so formed resemble in appearance, properties, and composition the bodies known as melanins and proposed for the artificially prepared bodies the name melanoidins.

The melanins are dark-colored amorphous pigments found in hair, skin, and the choroid coat of the eye and in pathological tissues such as sarcoma. They always contain carbon, oxygen, and nitrogen, and generally either iron or sulphur or both. They all agree in high carbon and low hydrogen content, but otherwise the composition varies according to the source. They do not give any of the reactions for proteins, nor so far as known any other special reactions. They are soluble in alkalies and are precipitated from such solutions by acids. In this, in general composition, color, and the absence of any distinctive reactions, the resemblance between the melanins and the humus bodies of the soil lies. The decomposition products of the melanins have been studied especially by Zdarek and Zeynek,[d] Berdez, Nencki and Sieber,[e] and Hoppe-Seyler,[f] but it is thought by some that the derivatives found by these may have been impurities in the original material examined. In any case there is at present no knowledge of the constitution of these bodies, nor even is it known whether they are mixtures or a group of closely related bodies. Spiegler[g] has pointed out that the melanins may show quite different chemical reactions from the melanoidins.

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[a] Zeitsch. physiol. Chem., **11,** 537 (1887); **12,** 33 (1888).

[b] Zeitsch. physiol. Chem., **13,** 66 (1889).

[c] Archiv. exper. Path. u. Pharm., **39,** 1 (1897).

[d] Zeitsch. physiol. Chem., **36,** 493 (1902).

[e] Archiv. exper. Path. u. Pharm., **20,** 346, 362 (1885); **24,** 17 (1888).

[f] Zeitsch. physiol. Chem., **15,** 179 (1891).

[g] Hofmeister's Beitr., **4,** 40 (1903).

The identity of melanins or natural pigments of animal origin with melanoidins or humus bodies is as yet undetermined, as might well be the case with what, so far as our present knowledge goes, may be mixtures of several amorphous bodies. The fact remains that these two groups of bodies are evidently closely related, and this convergence of two separate lines of investigation, one purely physiological and the other agricultural, till they meet in bodies closely related, if not identical, is of great interest.

Recent work on humus bodies is not very extensive, but what there is tends largely to discredit the claims of the bodies described by earlier workers to recognition as definite chemical compounds. For instance, Post[a] and Muller[b] point out that the humus bodies obtained from soils are often the chitin remains of insects, or the excrement of animals, and Korstyscheff[c] that these humus bodies may often be remains of bacteria and molds. In 1904, Malkomesius and Albert[d] published analyses of humic acids, so called, including the preparations of Merck and Krantz and a natural deposit known as Cassel brown. The figures obtained by them for hydrogen and carbon were approximately the same as those obtained by Detmer for humic acid from turf already quoted.[e] Schermbeck,[f] however, shows that the material analyzed and called humic acid by these authors was in large part a mixture of waxes and resins. As evidence of the variability of the so-called natural humus bodies the work of Cameron and Breazeale[g] may be cited, showing that the carbon in humus obtained in the usual way from a number of typical American soils varied in carbon content from 33.3 per cent to 50 per cent.

Two papers have recently appeared presenting research work on humus bodies which are particularly valuable contributions to our knowledge of these bodies, in that the problem is attacked from new points of view, and by methods not heretofore utilized in the study of these bodies.

Suzuki[h] reports results obtained by treating nitrogen-containing humic acid from different sources with boiling hydrochloric acid and then subjecting the solution obtained to esterification and fractional distillation according to the method of Fischer.[i] By this treatment he separated and identified the esters of most of the monamino and diamino acids and other decomposition products obtained on boiling protein bodies with acids and in addition obtained a quantity of unidentified acids. The conclusion drawn from this work is that humic acid consists for the most part of an insoluble body of a protein nature and that amino bodies are not present as such. The latter part of this conclusion would seem not to be warranted by the work as stated. It is quite possible for some of the decomposition products which were obtained to have been present, though doubtless in smaller amounts, in the humic acid before treatment with boiling acids and to have escaped detection by the tests made. The work, however, does prove that the humic acid examined by him was either of protein nature, a mixture of protein decomposition products, or probably both, together with some as yet unknown bodies.

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[a] Landw. Jahrbücher, 1888, p. 405.

[b] Studien über die natürlichen Humusformen, Berlin, 1887, p. 173.

[c] Annales Agronomiques, **17**, 17 (1891).

[d] Jour. prakt. Chem., **70**, 509 (1904).

[e] Jahresb. über Fortsch. Chem., 1873, p. 844.

[f] Journ. prakt. Chem., **75**, 517 (1907).

[g] Jour. Am. Chem. Soc., **26**, 43 (1904).

[h] Bul. Coll. Agr., Tokyo, **7**, 513 (1907).

[i] Zeitsch. physiol. Chem., **33**, 151, 412 (1901).

In a paper on the chemistry and physiological action of the humic acids[a] Robertson, Irvine, and Dobson report investigations into the chemical composition and constitution of humic acids. These authors obtained four preparations of humic acid—two natural, from peat by treatment with ammonium and potassium hydrate, respectively, and two artificial, by boiling sugar with hydrochloric acid and treating portions of the brown amorphous material so obtained with ammonia and potassium hydrate. They found some difference in composition of the natural preparations, that obtained through ammonia containing 54.24 per cent carbon, while that through potassium hydrate contained 56.67 per cent. The artificial preparations were almost identical in composition, except that the one obtained through ammonia contained 0.76 per cent nitrogen, while the other was nitrogen free. This nitrogen the authors speak of as combined, an assumption which, in view of the great absorptive power of humus bodies for ammonia, is not warranted in the absence of direct evidence of such combination. In these preparations the authors determined methoxyl, CH_3O, by the method of Zeisel[b] and found such a wide difference between the natural and artificial preparations in this respect that the only conclusion justified is that there are important differences in constitution, despite the general agreement of properties and composition. In the humic acid from peat 1.71 to 2.47 per cent CH_3O was found, while in that from sugar 6.47 per cent was obtained.

Considerable space in this paper is devoted to a discussion of the empirical formula of humic acid, but the discussion is based on the assumption that the bodies obtained in the manner stated and called humic acid are definite organic compounds, an assumption which is, as will be shown, questionable.

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[a] Bio-Chem. Jour., **2**, 458 (1907).

[b] Monatsh. Chem., **6**, 989 (1885).

DISCUSSION OF WORK ON HUMUS BODIES.

These results, obtained by investigations scattered over the last seventy years—results in many cases widely at variance with one another and viewed as a whole disconnected and fragmentary—are all that the student of the present day has presented to him in answer to the question, What do we know of humus organic matter in the soil? How much of this is true, how much erroneous, what shall be accepted and what rejected, are obviously questions that must be met at the outset. This has been met either consciously or unconsciously by all workers or writers in agriculture, in ways which may be summed up as follows:

A few agricultural writers accept some of the original names applied to humus bodies, notably humic acid, ulmic acid, and ulmin, and these names they use as though they were definite bodies of well-established composition and constitution. There is probably in the minds of these writers no definite idea of composition or constitution, or even any thought given to that side of the question, but the terms are used consistently and humates and ulmates are spoken of with the same certainty that one might speak of oxalates or citrates.

Other writers, the majority probably, if they have to speak of humus bodies as a class, state that they are probably complex mixtures of little-known bodies, but when they treat the broader subject of plant food and the function of humus in the soil they inconsistently speak of humates, ulmates, etc., with the same assurance as the first class.

A third class holds that the names applied by Mulder to humus bodies are names only; that the acid character of these so-called acids has never been demonstrated; and further, that there is no evidence that the bodies so designated are definite compounds, but rather in most cases that they are complex mixtures. The statement by Cameron and Bell[a] puts the case concisely, "The existence itself of these acids has never been demonstrated * * * No satisfactory descriptions of the physical or chemical properties of these supposed acids, their salts, or characteristic derivatives, have been recorded," and this view can not be too strongly emphasized. Most physiological chemists, to whom the unknown constitution and uncertain composition of humus bodies or melanoidins is the most prominent characteristic, not to speak of the resemblance to melanins, also bodies of unknown constitution and variable composition, likewise concur in this view.

Very brief consideration of the status of organic chemistry at that early time and of the enormous advance made since then, an advance which has given nearly all knowledge included in that branch of science at the present time, can not fail to convince one of the futility, not to say absurdity, of accepting unchallenged the findings of these early workers. Organic chemistry at that time was essentially elementary analysis—the determination of carbon, hydrogen, oxygen, and other elements—and observations on the ordinary physical properties of organic bodies. All other methods depended on at the present day for establishing the identity of organic compounds were unknown. The records of this early work give meager, if any, information regarding crystalline form of bodies themselves, or of their derivatives, and any mention of melting point or boiling point is lacking. All the present methods of addition, substitution, etc., by which organic compounds are arranged in classes according to structure were unknown or not recognized at their true value. Isomerism was not recognized and modern methods of molecular weight determination were not in use. It made no difference whether a body was amorphous or not, it was only necessary to have a mixture of bodies which remained somewhat constant through simple solution and precipitation, to find its percentage composition of carbon, hydrogen, and oxygen, record some of its common physical properties, and give it a name according to the fancy of the investigator, and it was established as a definite organic compound. If this body or mixture of bodies gave a precipitation with some mineral or alkaline earth, the precipitate was regarded as a salt and the organic mixture so precipitated was called an acid. Chlorophyll, protein, casein, gelatine—bodies regarding which our knowledge at the present day is very incomplete—were spoken of by Mulder and his contemporaries with the same certainty they assumed in regard to oxalic or citric acid, simply because they had all been subjected to elementary analysis and their common properties observed.

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[a] Bul. No. 30, Bureau of Soils, U. S. Dept. Agr., p. 39.

The striving of some of these early workers after simple relations between organic compounds based simply on elementary composition is one of the most prominent features of their work, and in this effort to classify compounds the statements they were led to make regarding bodies which we now know stand in no such relationship as they supposed is perhaps one of the best illustrations of the primitive nature of organic chemistry at that time, and a very convincing argument against accepting any of their work, unless verified in the light of our present knowledge. Speaking of vegetable acids, Mulder says:[a]

> Some acids exist in fruits, and it is worthy of remark that these bear all a simple relation to one another.
>
> Citric acid, $C_4H_2O_4 \times 3 = C_{12}H_6O_{12}$.
> Malic acid, $C_4H_2O_4 \times 2 = C_8H_4O_8$.
> Tartaric acid, $C_4H_2O_5 \times 2 = C_8H_4O_{10}$.
> Protartaric acid, $C_4H_2O_5$.

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[a] The Chemistry of Vegetable and Animal Physiology, trans. Fromberg, 1849, p. 805.

Again, in speaking of "gelatine sugar":[a]

> Sulphuric acid when acting on gelatine forms a kind of sugar containing nitrogen, represented by $C_8H_9N_2O_7$; if from this we subtract $C_6H_5O_5 = \frac{1}{2}$ equivalent of cane sugar, there remains $C_2H_4N_2O_2$ = urea,

a straining at a relationship between unrelated compounds which appears absurd to us now, but which is based on exactly the same kind of data and methods of reasoning as the relations stated to exist between ulmic, humic, and geic acids.

There is no reason to suppose that these early workers were not competent to perform elementary analyses, and the figures given for percentage composition may be received as accurate for the material analyzed, but there the accuracy stops. There is no reason for accepting the formulas given or for the assumption that the bodies examined are definite compounds. In fact, there is abundant evidence that such is not the case. There is, first, the amorphous, ill-defined nature of the bodies in question, not established as homogeneous by many modern methods available for such purpose; then the various and discordant figures for percentage composition obtained by different workers for what was supposed to be the same body; some evidence already quoted, obtained by workers of the present day, that these bodies really are mixtures; and, finally, very simple experimental evidence establishing this fact by which anyone can easily satisfy himself. If humus bodies be prepared from a soil in the usual way by extracting the soil with dilute alkali and precipitating these bodies from the solution so obtained by acid, there results, on thoroughly washing this precipitate, a body or mixture containing carbon, hydrogen, oxygen, nitrogen, and some ash ingredients. If this precipitate is again dissolved in alkali and precipitated again, there is obtained a mixture containing carbon, hydrogen, oxygen, and nitrogen in quite different proportions from the first precipitate. This can be repeated again and again, each time obtaining different results as to elementary composition. It is of interest to note in this connection that if this be repeated several times a point is reached where the humus precipitate becomes colloidal and passes through the filter. It is evident that by this procedure one could obtain as many humic acids as there were stages in the operation, although the composition varies less and less as one proceeds. In reality, the first precipitate is a mixture, and some of the bodies which seem to be held absorbed in this precipitate are removed by the subsequent operations and appear in the filtrates. This phenomenon is similar to that met with, for instance, in the analysis of the hydrochloric acid extract of a soil. In this case the bulky gelatinous precipitate of iron and alumina hydrates retain some of the lime, and this can not be removed by washing, but can be removed by dissolving the precipitate in acid and reprecipitating. Again, if the first precipitate obtained as above, the so-called humic acid, be treated with solvents, such as alcohol or ether, it is easy to obtain therefrom bodies or mixtures of quite different composition and properties from the original mixture. Further, in the case of the so-called artificial humic acid, for instance, that produced on heating sugar with hydrochloric acid, the composition of the resulting dark-colored amorphous body varies quite widely as influenced by concentration of the acid or length of time of heating.

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[a] Loc. cit., p. 233.

The only conclusion, then, that can be reached from this survey of the literature is that humic acid and allied bodies are mixtures of unknown compounds, and that if there is a single compound making up the major portion of the so-called humic acid, it is as yet of unknown composition, constitution, and properties, and that these bodies, whatever they may turn out to be, may be defined as those dark-colored amorphous compounds arising in soils through the decay of organic matter. In this group, then, would be included those soluble in alkalies, the so-called ulmic and humic acids, and also those insoluble in alkalies, known as ulmin and humin.

As doubtful as is the constitution or even composition of these supposed bodies, even more so is their action, harmful or otherwise, on plants, and no further discussion is called for by the purpose and scope of the present bulletin.

SEPARATION OF NONHUMUS BODIES.

The knowledge to be gleaned from a survey of the literature, of compounds other than these dark-colored mixtures discussed above is somewhat more definite in character. Crenic and apocrenic acid are the only nonhumus bodies recognized by Mulder and others of his day. These acids were first described by Berzelius[a] and further described by Mulder. The status of these bodies is exactly that of humic acid and other soil bodies described by Mulder, and all that has been said regarding the one class may be applied to the other. There is no evidence that any such definite organic compound of the composition and properties described exist in soils.

The possibility of there being other organic nonhumus bodies than these was early recognized, and, as has already been noted, played a part in the early discussion whether humic acid contained nitrogen as a component. It was not, however, until comparatively recent times that anything definite appeared along this line, and all the information so far obtained and suggested centers around the organic nitrogenous compounds. Among workers who contributed to the literature on the question of the character of the nitrogen in humus bodies may be mentioned Loges,[b] who found that a hydrochloric acid extract of a soil contained a nitrogen-holding humus body which yielded a precipitate with phosphotungstic acid, and Eggertz,[a] who found from analyses of thirteen samples of humus that the nitrogen content varied from 2.59 per cent to 6.43 per cent, and that it was present in organic combination, not as ammonia. This conclusion he based on the fact that the nitrogen could not be removed by repeated solution in alkali and precipitation with acids. The probability of the presence in soils of organic nitrogenous compounds not in combination with the humus apparently received very little attention until quite recently.

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[a] Pogg. Ann., **29,** 1 (1833).

[b] Landw. Vers.-Stat., **32,** 201 (1886).

Baumann[b] in 1887 suggested the presence of amino compounds in soils, basing the suggestion on the fact that on boiling soils with hydrochloric acid, ammonium compounds not originally present are formed. Berthelot and Andre[c] concluded from their investigations that the nitrogenous compounds in the soil were chiefly insoluble amids which are easily split into ammonia and soluble amids. Warrington[d] demonstrated the presence of small quantities of soluble amids in soils, and Sestini[e] showed that at least a portion of the soil nitrogen was present as amino acids. Dojarinko[f] obtained from Russian black soils large quantities of amino nitrogen. In 1905 Shorey[g] published results obtained by the application of the methods of Housmann,[h] as modified by Osborne and Harris,[i] to soil. The object of this method is a classification of the decomposition products obtained on boiling protein with strong acids and the results obtained indicate the presence of some of these decomposition products or compounds which give rise to them on boiling with acid. None of these investigations deal with the isolation or identification of any definite amino compound, but are merely attempts to classify a portion of the organic matter, and serve as an indication of what might be found in the soil, and neither the results obtained nor the methods used need be commented on here.

Considering now nitrogenous compounds not of an amino nature, Berthelot and Andre[j] obtained results on the distillation of soils which suggested to them the presence of a pyridine compound.

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[a] Meddelanden fran Konigl. Landbruks-Akademiens Experimentalfält. Stockholm, 1888, pp. 1-66; Centralbl. f. Agr. Chem., 1889, p. 75.

[b] Landw. Vers.-Stat., **33,** 247 (1887).

[c] Compt. rend., **103,** 1101 (1886).

[d] Chem. News, **55,** 27 (1887).

[e] Landw. Vers.-Stat., **51,** 153 (1899).

[f] Landw. Vers.-Stat., **56,** 311 (1902).

[g] Agr. Invest. Hawaii in 1905, Report of Chemist, p. 34.

[h] Zeitsch. physiol. Chem., **27,** 95 (1899).

[i] Jour. Am. Chem. Soc., **22,** 323 (1900).

[j] Compt. rend., **112,** 598 (1891).

Recently Shorey[a] has isolated from an Hawaiian soil a pyridine compound, picoline carboxylic acid, which appears to be the first isolation and identification of a definite crystalline organic compound from a soil.

Of the isolation of nonhumus compounds not containing nitrogen there is no mention in the literature except statements that humic acid, as originally obtained, often contains waxes and resins, and that compounds like acetic acid, formic acid, alcohol, etc., have been detected.

Summing up this survey of the literature, it might be stated that the most conspicuous feature is lack of specific knowledge concerning the organic matter of the soil. The humus bodies are a group of compounds of unknown composition and constitution, some of which seem to resemble the natural animal pigments known as melanins, themselves bodies of indefinite composition and unknown constitution, apparently of a protein nature. There is some evidence that amino compounds are present in certain soils, but beyond this there is no knowledge what members of this large group of nitrogenous bodies may be present. The presence of waxes, resins, and other difficultly decomposable plant residues is indicated, and finally there is the isolation of a single nitrogenous compound picoline carboxylic acid, which doubtless constitutes but a very small portion of the organic matter.

It may not be out of place to remark that this ignorance concerns an important soil ingredient, the presence of which makes soil out of what would otherwise be rock powder or sand. As has been stated in a previous bulletin,[b] the amount of organic matter in ordinary soils is appreciably large, for as the result of analyses of several thousand samples of soil from all parts of the United States, Cameron[c] has shown that the average organic content of soils is 2.06 per cent and of subsoils 0.83 per cent. If the soil be taken as 8 inches deep, there would be an average of 28 tons of organic matter in the soil per acre and 50 tons in the soil and subsoil to the depth of 2 feet.

There are, then, in most soils tons of organic matter, matter which is constantly being changed through the activity of micro- and macro-organisms, through cultivation and fertilization; matter which includes bodies harmful to vegetation, other bodies probably beneficial, and still other bodies wholly inert, but matter about which there is very little chemical knowledge.

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[a] Report Hawaii Agr. Expt. Sta., 1906, p. 37.

[b] Bul. No. 47, Bureau of Soils, U. S. Dept. Agr., p. 10.

[c] Jour. Am. Chem. Soc., **27**, 256 (1905).

EXPERIMENTAL METHODS.

The problem which the student of soil fertility has to face may now be stated tentatively as follows: Many soils are infertile because of the presence in them of organic matter inhibitory to crops. Of this organic matter, which is presumably relatively small in amount, nothing definite is known chemically. Not only this, but on a survey of the investigations into the nature of soil organic matter which have been carried on in the last seventy years it is found that there is nearly a total absence of the proof of the presence of any definite organic compound in the soil, either harmful or otherwise. How can some knowledge be obtained of the chemical nature and properties of these bodies, that there may be intelligent treatment of soils containing them, treatment that will bring about certain destruction or change of the harmful bodies, or prevent their formation, instead of the rule-of-thumb methods now in use. Obviously one way to attain this knowledge is to isolate these bodies from soils and study their properties.

To anyone who realizes the paucity of knowledge of soil organic matter, which has been emphasized in previous pages, it will be apparent that the isolation of any definite organic compounds from the soil is not an easy task. When the task is narrowed down to the isolation of injurious compounds, the difficulties are greatly increased. Before outlining the methods by which this problem has been approached, some of these difficulties should be considered, for the matter resolves itself into a choice of methods to surmount these difficulties.

It is evident, in the first place, that for any organic soil compound to be harmful to plants it must be present in the soil solution; that is, it must be at least slightly soluble. Investigations have shown that many organic compounds stated in the literature to be insoluble are soluble to the extent of a few parts per million at least, and sufficient in many cases to have a harmful effect on plants grown in the solution. The water extract of an infertile soil usually contains but a very small quantity of organic matter, and it is a reasonable presumption that the injurious organic compound is only a part of the total organic matter present. Such being the case, it is evident that the isolation of any organic compound from a water extract of a soil in sufficient amount to establish its identity and study its properties is in most cases a problem that does not come within the limitations of laboratory work. In other words, the amount of soil or soil extract necessary to handle would be too great for ordinary laboratory appliances and methods. This difficulty, due to the small quantity of organic material which must be present in the soil solution, is much increased by the fact that the inhibiting substances are unknown compounds with unknown chemical and physical properties. In many respects the isolation of an injurious substance from an infertile soil and the detection in animal organs of a poison of which the identity, properties, characteristic reactions and symptoms produced are all unknown, are analogous.

With the water extract of a soil practically unavailable as a source of the unknown compounds under the present limitations of laboratory work, and with the lack of methods applicable to such research, the only course open is to make use of all other methods which are known or can be devised for the solution of the soil organic matter, and to attempt to isolate from such solution definite compounds, taking advantage of proven methods, or devising new ones.

Before stating the methods which have been used with different soils in the attempt to isolate from them organic bodies, and the results obtained thereby, there are a few facts regarding the soil organic matter which are true more or less for any soil and which should be kept in mind throughout the discussion of the subject. The organic matter in soils is generally but little soluble at ordinary temperatures in neutral solvents, such as alcohol, ether, or chloroform. Dilute acids at ordinary temperatures have also little solvent action on soil organic matter, and if heated there is usually a change effected in the constitution of some of the organic bodies. Dilute alkalies at ordinary temperatures dissolve relatively large quantities of soil organic matter; in fact, in the case of some soils, nearly the whole of the organic matter can be so dissolved by repeated treatments. This treatment of soils with dilute alkalies, although it may in some cases effect a change in the constitution of some of the organic compounds, especially those nitrogenous, seems at present the only method of effecting the solution of a large part of the organic matter with the minimum chance of changing the character of the compounds sought, and for this reason was the first method used in the attempt to isolate harmful organic bodies from the soil.

SEPARATION OF PICOLINE CARBOXYLIC ACID.

The soil first treated in this way was from Takoma Park, Md., and is fully described in a former bulletin.[a] This soil, which is characterized physically by large percentages of clay, silt, and coarse sand, and very little of the intermediate material, is quite light in color and contains, contrary to what might be expected from its appearance, 3 per cent organic matter. It contains 0.1 per cent nitrogen, and analyses of both water and acid solutions indicate the presence of sufficient mineral plant food for ordinary crops. It is, however, an exceedingly infertile soil and does not respond readily to treatment with either stable manure or commercial fertilizers. A bacteriological examination of a sample of this soil by Mr. Karl F. Kellerman, of the Bureau of Plant Industry, showed this to be rather low in bacterial content though active in denitrification.

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[a] Bul. No. 28, Bureau of Soils, U. S. Dept. Agr.

The water extract of this soil is a poor medium for the growth of wheat seedlings, but is much improved by treatment with carbon black, by dilution, and by the addition of pyrogallol or calcium carbonate. In other words, field observations of this soil indicate that something other than lack of plant food is the cause of infertility, and laboratory observations confirm this and in addition indicate that this infertility is due to the presence of some harmful substance.

When the soil is treated with a 2 per cent solution of sodium hydrate there results a dark-colored solution, the so-called humus extract. If this solution after separation from the soil residue be treated with an excess of acid a flocculent dark-colored precipitate is formed, the so-called humic acid. The filtrate from this is dark colored but much lighter than the original extract and contains a portion of the organic matter. On bringing this extract to neutrality by the addition of sodium hydrate there is formed a further precipitate containing both organic and mineral matter. The neutral filtrate from this is still colored dark yellow and contains a considerable portion of the organic matter originally extracted from the soil by sodium hydrate. By dissolving both of the above precipitates again in sodium hydrate and repeating the operations of acidifying, filtering, neutralizing, and again filtering, there can be obtained a still further quantity of organic matter in neutral solution, which can be mixed with the first portion.

This process results in a neutral solution containing some of the organic matter and a comparatively large amount of a sodium salt resulting from the neutralization of the sodium hydrate used. This neutral solution of soil organic matter gives precipitates upon the addition of a number of mineral salts such as basic lead acetate, cupric acetate, mercuric nitrate, and silver nitrate, precipitates which contain organic matter and are usually nitrogenous.

In this method of obtaining a neutral solution of soil organic matter, the amount so obtained in solution seems to be approximately the same, whether hydrochloric, sulphuric, or nitric acid be used for neutralizing; acetic acid, however, usually gives a smaller amount in solution than the mineral acids. The final treatment to which the solution is to be subjected must decide what acid is used throughout, e. g., hydrochloric acid would not be used if there were any intention of using silver nitrate as a precipitant, nor sulphuric acid if lead subacetate was to be used.

METHOD OF ISOLATION.

The method finally adopted for this particular soil was to treat it for twenty-four hours with frequent shaking with 2 per cent solution of sodium hydrate free from chlorides, allowed to stand until the soil residue settled and the dark-colored solution siphoned off. To this was added a slight excess of nitric acid free from the lower oxides of nitrogen and the flocculent humus precipitate filtered off. The acid filtrate was then exactly neutralized by the addition of sodium hydrate and the precipitate so formed filtered off. To the resulting neutral solution was added a solution of silver nitrate and the precipitate formed, which was slight in amount, was allowed to settle, the clear liquor decanted, and the precipitate collected on a filter and washed with a small quantity of water. The precipitate while still moist was suspended in water and treated with hydrogen sulphide, the silver sulphide filtered off, and the filtrate evaporated to small volume on a water bath and allowed to cool slowly. There was thus obtained a more or less colored residue in which crystals formed. The crystals were separated from the mother liquor, washed with a small quantity of cold water, dissolved in hot water, and precipitated again with silver nitrate. Filtration, treatment with hydrogen sulphide, etc., being now repeated, the crystals were usually obtained fairly free from color and could be further purified by recrystallization from water.

PROPERTIES OF THE ISOLATED COMPOUND.

The crystals obtained are little soluble in cold water, easily in hot, little soluble in alcohol, and almost insoluble in ether. From water the compound separates in oblique prismatic crystals with water of crystallization which they lose at 100° C. In Plate I, figure 1, is shown a photomicrograph of these crystals obtained by allowing a rather dilute solution in hot water to cool slowly, and figure 2 shows the crystals obtained by cooling a rather concentrated solution in water. The latter crystals are usually very thin plates, superimposed, forming large scale-like masses and giving very brilliant color effects with polarized light. The substance sublimes unchanged on heating in an open dish and does not melt in a capillary tube at 300° C. A water solution is faintly acid to litmus, and when neutralized does not give a precipitate with either barium chloride, calcium chloride, cadmium sulphate, or lead acetate. Cupric acetate gives a bluish crystalline precipitate, insoluble in cold water. Silver nitrate gives a flocculent amorphous precipitate.

IDENTIFICATION AS PICOLINE CARBOXYLIC ACID.

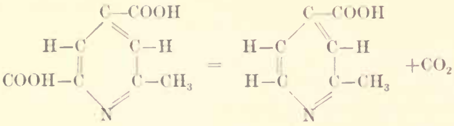
The crystals have, therefore, the appearance and properties of picoline carboxylic acid, which, as stated, had been isolated by Shorey from a Hawaiian soil by the same method. The compound from Hawaiian soil was further identified as picoline carboxylic acid by its corresponding water of crystallization, its nitrogen content, the chlorine content of the hydrochloride, and its conversion into lutidinic acid on oxidation. The last-named acid is characterized by crystallizing in leaflets little soluble in cold water and melting at 239° C., and giving a yellowish or orange color with ferrous sulphate.

The preparation obtained from the Takoma soil having the properties stated above was compared with that obtained from Hawaiian soil, and also with picoline carboxylic acid prepared artificially in the laboratory, and found to correspond throughout.

PICOLINE CARBOXYLIC ACID AND RELATED COMPOUNDS.

Picoline carboxylic acid, which has heretofore been known as a laboratory product only, has been described by Böttinger[a] and can be prepared by heating uvitonic acid to 274° C. Uvitonic acid, which is methyl pyridine carboxylic acid, breaks up at this temperature into carbon dioxide and picoline carboxylic acid, as shown below:

Uvitonic acid. Picoline carboxylic acid.



Uvitonic acid can be easily prepared in the laboratory by treating pyruvic acid with alcoholic ammonia, separating the precipitate formed, washing it with ether, dissolving it in water, and precipitating the free acid by the addition of sulphuric acid, as described by Böttinger.[b]

Leaving the toxicity of picoline carboxylic acid for discussion in subsequent pages in connection with other substances found in soils, it may be said here that it was found to be not very harmful to wheat seedlings, while the nearly related uvitonic acid was quite so. While this slight harmful effect and the apparently very small amount of this body in the Takoma soil make it improbable that it is responsible for more than a small part of the infertility of that soil, its close connection with the uvitonic acid and other closely related acids, such as pyridine tricarboxylic acid,[a] known to be antiseptic, justifies the suspicion that there may be present some other pyridine compound either a source of or a product of the one actually found and one which might be the active cause of infertility.

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[a] Ber. chem. Ges., **14**, 67 (1881); **17**, 92 (1884).

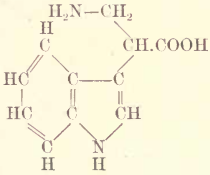
[b] Ann. Chem., **188**, 330 (1877); **208**, 138 (1881); Ber. chem. Ges., **13**, 2032 (1880).

POSSIBLE ORIGIN OF PICOLINE CARBOXYLIC ACID.

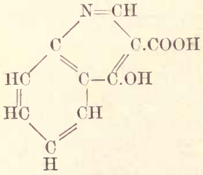
Regarding the origin of the picoline carboxylic acid in the soil, very little can be said at the present time, yet it may not be out of place to call attention to a few facts in connection therewith. In the laboratory picoline carboxylic acid can be formed from pyruvic acid and ammonia through the intermediary compound, uvitonic acid, by splitting off carbon dioxide. Pyruvic acid has been shown by Mörner [b] to be a constant secondary decomposition product of protein, and as such might be formed in the soil; in fact, there are some indications of its presence along with picoline carboxylic acid in the soil under investigation. Should this be the case, then it is not impossible that the remaining steps in the formation of picoline carboxylic acid should take place in the soil, although no reaction whatever for the uvitonic acid could be obtained. The most that can be said, therefore, is that the picoline carboxylic acid may possibly have arisen as the result of the splitting and decomposition of protein in the soil.

A further point of interest in regard to the formation of the pyridine nucleus in the soil through the decomposition of protein is shown by the formation of pyridine on reduction of the melanoidins or humin substances, resulting from the dissociation of protein, as demonstrated by Samuely.[c] Hopkins and Cole[d] have further shown that tryptophane, one of the dissociation products of protein, is readily changed to dark-colored humin substances on boiling with acids, or even with water, and Ellinger[e] has suggested for trytophane the structural formula:

Tryptophane.



Kynurenic acid.



which, as is readily seen, contains the possibility of the pyridine closure, as illustrated by its transformation into kynurenic acid. All

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[a] Rademaker, Med. Herald, **19,** 107 (1887).

[b] Zeitsch. physiol. Chem., **42,** 121 (1904).

[c] Hofmeister's Beitr., **2,** 355 (1902).

[d] Jour. Physiol., **27,** 418 (1901); **29,** 451 (1903).

[e] Zeitsch. physiol. Chem., **43,** 325 (1904).

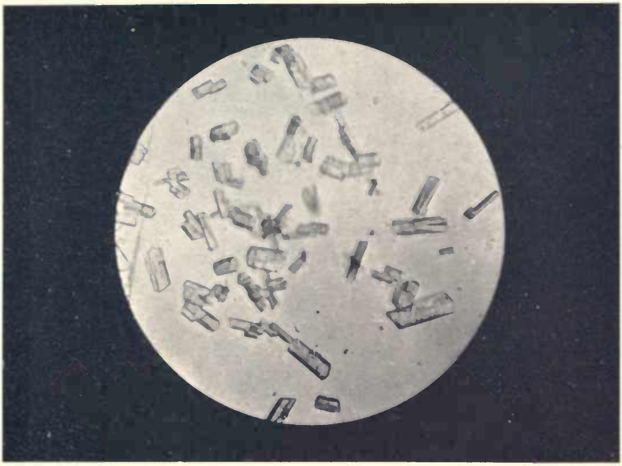

FIG. 1.—CRYSTALS OF PICOLINE CARBOXYLIC ACID OBTAINED FROM SOILS, FORMED FROM A DILUTE AQUEOUS SOLUTION.

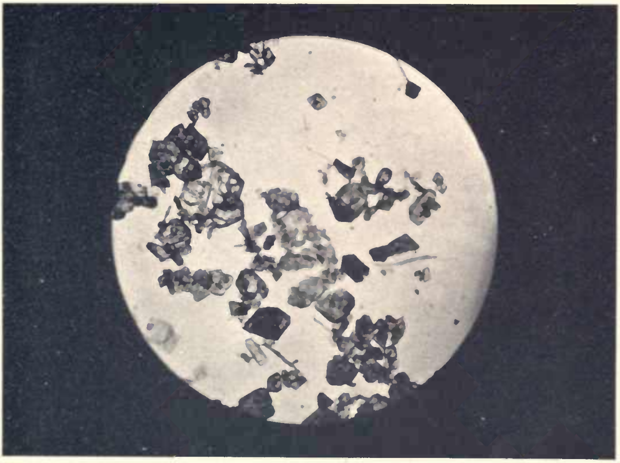

FIG. 2.—CRYSTALS OF PICOLINE CARBOXYLIC ACID OBTAINED FROM SOILS, FORMED FROM A CONCENTRATED AQUEOUS SOLUTION.

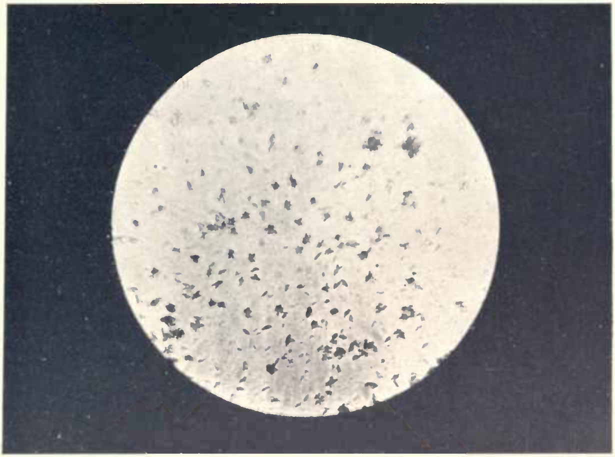

FIG. 1.—CRYSTALS OF DIHYDROXYSTEARIC ACID OBTAINED FROM SOILS.

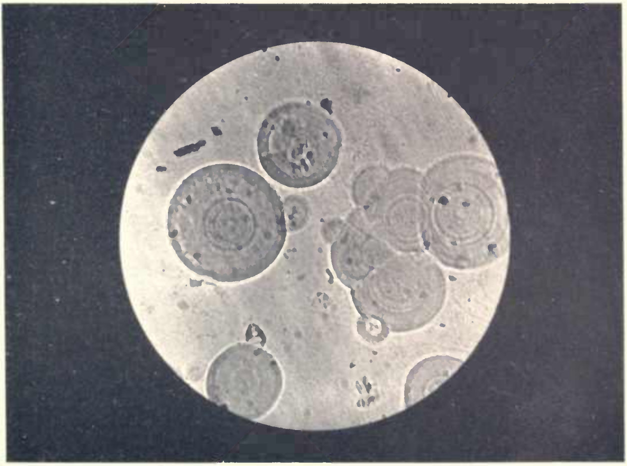

FIG. 2—CONCRETIONS OF THE BARIUM SALT OF DIHYDROXYSTEARIC ACID.

these facts indicate strongly that the origin of the pyridine ring in the soil, whether it be as picoline carboxylic acid or other pyridine derivative, lies most probably in the decomposition of protein bodies.

THE PRESENCE OF OTHER COMPOUNDS INDICATED.

There has been gathered some evidence of the presence of pyruvic acid in the Takoma soil, but this evidence is as yet indicative only. This evidence, stated briefly, is as follows: When the neutral soil extract obtained as outlined above is made alkaline with sodium hydrate and then a solution of iodine in potassium iodide added there is formed in a short time at room temperature a precipitate of iodoform. The same precipitate can be obtained by treating the original sodium hydrate extract of the soil with iodine reagent. The iodoform so obtained was identified, after recrystallizing, by its melting point and by its characteristic crystalline form as well as its odor. Pyruvic acid forms iodoform when treated in this way, but this is true of other acids, for instance, lævulinic. Again, when the neutral soil extract is made acid and treated with a solution of phenylhydrazine hydrochlorate there is produced in a short time a reddish-colored micro-crystalline precipitate which soon tends to become resinous. It was not found possible by any means so far tried to purify this precipitate so as to obtain any characteristic crystalline form or constant melting point. The phenylhydrazone of pyruvic acid crystallizes in needles and melts at 178° to 183° C. It is evident that if pyruvic acid is present there is also present another compound giving a precipitate with phenylhydrazine. Bülow[a] has described a reaction of the phenylhydrazones which he states is characteristic. When the phenylhydrazone is treated with concentrated sulphuric acid and dichromate of potassium there is produced a purplish color. This color is produced by the phenylhydrazone precipitate from the soil extract and by the pure phenylhydrazone of pyruvic acid.

Simon[b] has described a color reaction of pyruvic acid which he states is characteristic. This depends on the blue color given by sodium nitroprusside and ammonia when added to dilute solution of pyruvic acid. When the neutral soil extract is treated with these reagents there is produced a very slight greenish color, which, since the soil extract is orange colored, might be expected in the presence of small amounts of pyruvic acid. The delicacy of the reaction was tested by adding known quantities of pyruvic acid to the neutral soil extract and adding the reagents, and it was found that the reaction was not at all delicate in the presence of the other material present in the soil extract, as much as 500 parts per million being required to give the characteristic blue color, lower concentrations producing greenish shades. These reactions indicate at least the probable presence of pyruvic acid as well as other bodies not yet isolated.

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[a] Ann. Chem., **236**, 195 (1886).

[b] Compt. rend., **125**, 534 (1897).

Pyruvic acid was found to be quite injurious to wheat seedlings, but was not so when neutralized with sodium hydrate, and if present in the soil its activity as a factor in infertility would no doubt depend on the form in which it might be present. Apart from this the possible presence of this acid in the soil is of interest, for it may be that through the agency of ammonia in the soil the change from the open chain nonnitrogenous pyruvic acid to the ring form nitrogenous uvitonic acid could be effected, as is done in the laboratory with alcoholic ammonia. Uvitonic acid has been sought for in the various soil extracts, but so far with no indication that it is present.

When picoline carboxylic acid is prepared from the neutral soil extract by the method stated above there is separated from the crystals a dark-colored mother liquor containing nitrogen. When this is evaporated nearly to dryness there usually separates a further small quantity of picoline carboxylic acid, but no other crystalline body has been obtained or observed. The mother liquor at this stage, however, is thick and viscous and of such a nature that crystallization of any body present would be difficult. When the mother liquor is evaporated completely to dryness and then taken up again with water there is found a quantity of amorphous colored matter which does not redissolve.

When the dry residue obtained by evaporating the mother liquor to dryness is heated with caustic lime there is given off an odor of crude pyridine, indicating a still further quantity of picoline carboxylic acid or of some other pyridine compound. When the mother liquor from which picoline carboxylic acid has been separated is made alkaline with sodium carbonate and treated with a solution of diazo sulphanilic acid, a dark-red color is slowly formed. The color produced by this reagent with certain organic compounds was first noticed by Ehrlich[a] and further described by Pauly,[b] who found that it could be used for the detection of histidine in the absence of tyrosine. Histidine gives with this reagent a dark-red color which remains red on dilution, and no other protein decomposition product except tyrosine gives this color, all others giving yellow colors which disappear on dilution. According to Pauly the distinctive color given by histidine and diazo sulphanilic acid is due to the imidoazol group, histidine being α-amino β-imidoazol propionic acid. The color obtained by treating this soil material with diazo sulphanilic acid does not appear to be that obtained with histidine, being slower in appearing and soon losing the red tint on dilution. The same color can be obtained in the distillate on distilling the original soil with steam, and is much more pronounced if the soil be made slightly alkaline before distillation. Other organic compounds than those mentioned in the literature were found to give this color, for instance, arbutin[a] and piperidine, so that the most that can be said of this reaction is that it indicates the presence of some body not yet isolated or identified.

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[a] Zeitsch. klinische Med., **5**, 285 (1882).

[b] Zeitsch. physiol. Chem., **42**, 508 (1904); **44**, 159 (1905).

SEPARATION OF DIHYDROXYSTEARIC ACID.

The comparatively slight harmful effect of picoline carboxylic acid, the only compound up to this point isolated from the Takoma soil, coupled with the apparently very small quantity present in this soil, led to the conclusion that there must be some substances of much more injurious character than this present—substances perhaps not in any way connected with the one obtained or others indicated. With the object of, if possible, obtaining such other bodies from this soil a number of other methods were tried.

METHOD OF ISOLATION.

One which finally gave definite results was as follows: The soil was treated with 2 per cent sodium hydrate solution as in the method first used. This alkaline extract was made acid with a slight excess of acetic acid and filtered from the humus precipitate. There was thus obtained a dark-colored extract containing organic matter, sodium acetate, acetic acid, and some mineral matter from the soil. This acid extract was shaken out with ether and the ether allowed to evaporate on the surface of a small quantity of water in a warm place. The ether on evaporating left on the surface of the water some colored resinous material, together with nodules or concretions of a crystalline body. On heating the water to boiling these crystals went into solution, while the resinous matter remained undissolved, and on pouring the solution into a filter previously wet with hot water the resinous material remained in the filter. On cooling the solution so obtained, crystals separated, which generally appeared as very small plates or leaflets arranged in radiating clusters. These if still colored could be purified by solution in hot water and filtering as before. This body, which is white when pure, melts at 98° to 99° C., is little soluble in cold water, somewhat readily in hot, and quite soluble in alcohol or ether. A water solution is acid to litmus and decomposes barium or calcium carbonate, forming the corresponding salts, which are difficultly soluble in cold water. This body was found to be quite harmful to wheat seedlings.

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[a] Bul. No. 47, Bureau of Soils, U. S. Dept. Agr.

ISOLATION FROM SEVERAL SOILS.

With the object of extending the research to other soils, six more or less infertile soils, selected from near Arlington, Va., Indianapolis, Ind., Center Hall, Pa., State College, Pa., Pulaski, Tenn., as well as that from Takoma, Md., were treated as follows: Eight hundred grams of each were treated with 2,000 c. c. of a 2 per cent sodium hydrate solution for twenty-four hours, with frequent shaking; after standing, 1,000 c. c. of the supernatant clear extract was treated with a slight excess of acetic acid and filtered. The filtrate was shaken out twice with ether and the ether allowed to evaporate on the surface of a small quantity of water, the water boiled and filtered, and the filtrate cooled. The character of any crystals which formed and the approximate amount was observed. From four of the soils examined there was obtained crystalline material having the same general appearance and properties as that obtained by this method from the Takoma soil as described above. The amount of this material obtained from 1,000 c. c. of the original extract was then dissolved in water and made up to 1,000 c. c. with distilled water and used as a culture medium for wheat seedlings. Dilutions of this stronger solution with one and with nine parts of pure distilled water were also used. The results obtained were in direct relation to the amount of crystalline material, the solution containing the greatest portion being the most harmful. The results obtained with one of the soils, that from Tennessee, are shown in Plate III, figure 2.

The soil from which, by this treatment, the most material was obtained and which furnished the most injurious medium was from Tennessee, a soil which had been in cultivation fifteen years, for the most part in cotton. This soil is classified as Clarksville silt loam, and although light colored, contains 3.26 per cent organic matter and 0.16 per cent nitrogen. The surface soil (which was collected) is a gray silt loam 6 inches deep. The subsoil to a depth of 3 feet is yellow silt loam, having a close, compact structure. The field is in a large area of this type, the Clarksville silt loam, occupying the broad, nearly level top of a ridge. There were a few apple trees in the field, but the sample was taken at some distance from any of them. The yields have been light. On an area about 50 feet square, from which the sample was taken, the plants were only about one-half to one-fourth as large as in other parts of the field, and matured very few bolls. Where vacancies occurred in the cotton rows, corn had been planted. The same difference existed in the corn as in the cotton. Near where the sample was taken the stalks were small, with a yellow color, and had failed to form good ears. In other parts of the field the corn had a good color and average-sized ears had been produced. The east half of the field contains 20 apple trees, set five years ago. One tree stands about 30 feet from where the sample was taken and is smaller than the trees farther away, thus agreeing with the growth of the cotton and the corn in different parts of the field.

A water extract of this soil was a poor medium for the growth of wheat seedlings and was improved by treatment with carbon black.

Having, then, a soil unproductive in the field and in the laboratory, and yielding by simple treatment a crystalline body injurious to plant growth, the foundation was laid for the isolation of a harmful soil compound in sufficient quantity to determine its identity and study its properties. Large quantities of this soil were treated by the method already mentioned, extraction with 2 per cent sodium hydrate solution, acidifying with acetic acid, filtering from the humus precipitate, shaking out the acid filtrate with ether, and crystallizing the water-soluble portion of the ether extract from water. By this treatment, extracting each portion of the soil twice, the body described was obtained in a fairly pure condition in amounts of 0.05 gram per kilo of soil, which is 50 parts per million, or 200 pounds per acre to the depth of 1 foot. The quantity actually present in the soil must of course be much larger, for when all is said, the methods of extraction are very crude and far from quantitative, and the amount obtained in crystalline form does not even represent the amount extracted. It is of course impossible to say what relation exists between the amount extracted and the amount present, except that the amount present is much the greater, perhaps even several times as great. This same body has been obtained by extraction with sodium carbonate instead of hydrate, though the extraction is not so profitable.

PROPERTIES OF THE ISOLATED COMPOUND.

The properties of this compound, some of which have already been noted, are:

Slight solubility in cold water, more ready solubility in hot, ready solubility in alcohol and ether. It crystallizes in radiating clusters or concretions and when pure in very small plates or leaflets, which are generally arranged in starlike groups, as shown in the photomicrograph in Plate II, figure 1. The melting point is 98° to 99° C.

Calcium and barium salts are readily formed by decomposition of the corresponding carbonates. These are little soluble in cold water, but quite readily so in hot water. The barium salt crystallizes in somewhat characteristic circular concretions of radiating structure, as shown in the photomicrograph in Plate II, figure 2. The silver salt is amorphous and quite insoluble in water.

IDENTIFICATION AS DIHYDROXYSTEARIC ACID.

All the properties of this compound agree with those of dihydroxystearic acid prepared from elaidic acid. Elementary analyses of the preparation from the soil gave the following figures:

	No. 1 found.	No. 2 found.	Calculated for $C_{18}H_{36}O_4$.
Carbon	67.5	68.0	68.3
Hydrogen	12.2	11.7	11.4
Oxygen	20.3	20.3	20.3

Analysis of the silver salt gave the following figures:

	Found.	Calculated for $C_{18}H_{35}AgO_4$.
Silver	25.77	25.53

The melting point of the soil compound remained unchanged when this was mixed with dihydroxystearic acid prepared from elaidic acid.

These figures, together with the correspondence noted between the properties of the body obtained from the soil and those of dihydroxystearic acid from elaidic acid, are sufficient to establish the identity of the soil compound as dihydroxystearic acid.

DIHYDROXYSTEARIC ACID AND RELATED COMPOUNDS.

There are four isomeric dihydroxystearic acids known, three being laboratory products. The one found in the soil is that obtained in the laboratory by the oxidation of elaidic acid and described by Saytzeff.[a] This acid can easily be prepared, starting with oleic acid. If oleic acid be treated for a few minutes at a low temperature with nitrous oxide generated in any convenient way, say by the action of nitric acid on arsenic trioxide, it is changed to the isomeric elaidic acid. This, after washing with water and recrystallizing from ether or alcohol, melts at 45° to 47° C. If this elaidic acid be dissolved in a dilute solution of potassium hydrate and treated with potassium permanganate, it is oxidized, dihydroxystearic acid being one of the products. The yield obtained in this way is low, the dihydroxystearic acid first formed being easily subject to further oxidation, pelargonic and azelaic, and finally oxalic acids being formed. Edmed[b] in studying the oxidation products of oleic and elaidic acids obtained from the latter by this treatment with alkaline permanganate, dihydroxystearic acid, 33 per cent; pelargonic acid, 13 to 14 per cent; azelaic acid, 26 per cent; and oxalic acid, 15 to 20 per cent. The dihydroxystearic acid formed from elaidic acid is much more easily oxidized than the isomeric acid obtained by oxidation of oleic acid, and this has been explained by the juxtaposition of the hydroxyl groups in the former, as shown in the structural formulas:

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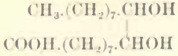
[a] Jour. prakt. Chem., **33,** 300 (1886); **50,** 76 (1894).

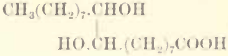
[b] Jour. Chem. Soc., **73,** 627 (1898).

Dihydroxystearic acid, m. p. 99°, from elaidic acid.



$$\begin{array}{r} CH_3.(CH_2)_7.CHOH \\ | \\ COOH.(CH_2)_7.CHOH \end{array}$$

Dihydroxystearic acid, m. p. 134°, from oleic acid.



$$\begin{array}{l} CH_3(CH_2)_7.CHOH \\ \quad | \\ \quad HO.CH.(CH_2)_7COOH \end{array}$$

The known dihydroxystearic acids other than that obtained by the oxidation of elaidic acid and found in soils are that obtained by the oxidation of oleic acid already mentioned, melting at 134° C.; one obtained from isoleic acid melting at 79° C., and a natural product found in castor oil melting at 140° to 141° C., and described by Juillard [a] and Meyer.[b] Besides the differences in melting points noted, these acids show quite important differences in their behavior toward solvents, but all agree in being little soluble in cold water. They are all monobasic acids, forming well-defined salts.

PRESENCE OF OTHER BODIES.

In describing the method used in isolating dihydroxystearic acid from the soil, mention was made of a resinous body which was present in the ether extract and which was separated from the dihydroxystearic acid after evaporation of the ether by filtration of the hot solution. This resinous material, which at the temperature of boiling water is a brown oil, becomes at room temperature a thick viscous mass. It is not soluble in water or dilute acids. In dilute alkalies it forms a slimy emulsion and dissolves readily in alcohol and ether. So far no crystalline body has been obtained from this material, nor has it been possible to make any crystalline derivatives. No characteristic color or other reactions have been noted, and it is not known whether it is a simple body or a mixture. Elementary analysis gave the following figures: Carbon, 63.84 per cent; hydrogen, 9.65 per cent.

It is very insoluble in water and when wholly free from dihydroxystearic acid it does not impart any harmful properties to distilled water, using wheat seedlings.

POSSIBLE ORIGIN OF DIHYDROXYSTEARIC ACID.

Concerning the possible origin of dihydroxystearic acid in the soil, it might not be amiss to state briefly some of the results obtained, although no definite conclusion can as yet be drawn. Among the soils containing this compound was the Takoma soil, from which picoline carboxylic acid had also been isolated. This soil was found to contain dihydroxystearic acid in almost as large amount as that from Tennessee. This Takoma soil seems to be an extremely good medium for the growth of fungi, and it was noted that the rootlets of the oak trees on this ground were infested with mold. This growth was at times so abundant that in digging up the small roots and shaking free of soil, the attached mold mycelia furnished as much material as the roots themselves. A quantity of these roots with mold attached was washed free of adhering soil and treated just as the soil had been in the isolation of dihydroxystearic acid. There was obtained in this way a small quantity of crystalline material having the appearance and properties of the dihydroxystearic acid isolated from the soil. The crystalline form, melting point, solubility, formation, and appearance of barium salt all corresponded with those of the body isolated from the soil, and there is little or no doubt of their identity. Similar oak roots from another locality where they were not infested with mold were treated in the same way, but no indication whatever was obtained of the presence of dihydroxystearic acid or any other crystalline body by this method. It would seem to be a fair conclusion from this that mold can form dihydroxystearic acid from material associated with oak roots, and that in this case, at least, the dihydroxystearic acid found in the soil may have been formed in this way. As to what material furnishes the foundation for this formation of dihydroxystearic acid by fungi, whether it be root excretions or root tissue or cells, it is possible at present to theorize only, and such discussion does not come within the scope of this paper. It may, however, not be out of place to mention that the conditions existing in nature in this case are similar to those shown in the laboratory to lead to the formation of dihydroxystearic acid. Oleic acid as part of the complex molecules of fats and readily decomposed lecithins is present in all living parts of plants; nitrous acid, by which oleic acid is changed to elaidic acid, is constantly being formed in soils, either as a product of denitrification or as one of the stages in nitrification; and, finally, there are oxidizing agents—the air, enzymes in living roots, and microorganisms.

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[a] Bul. Soc. Chim., **13,** 238 (1895).

[b] Arch. Pharm., **235,** 184 (1897).

SEPARATION OF OTHER ORGANIC COMPOUNDS FROM SOILS.

In the course of the examination of other soils for the presence of the compounds already described there have been obtained a number of bodies, some of which are undoubtedly mixtures, while others are evidently single, definite compounds. Two of these latter have been sufficiently studied to be mentioned here. The soil from which these bodies were obtained was from North Dakota, the Marshall clay, a black soil similar to the chernozen of Russia, containing 10.6 per cent organic matter and 0.51 per cent nitrogen.

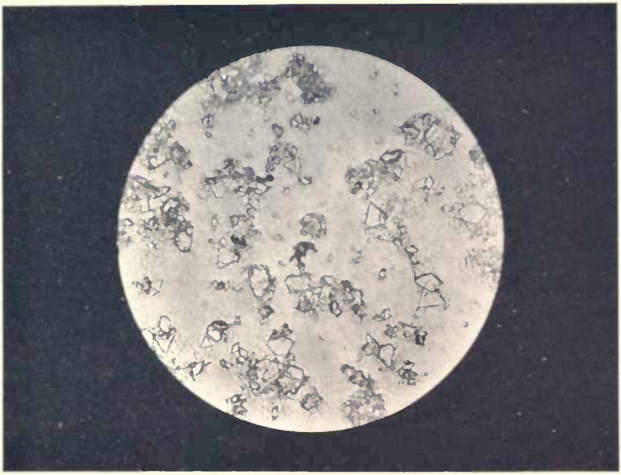

FIG. 1.—CRYSTALS OF AGROSTEROL OBTAINED FROM SOILS.

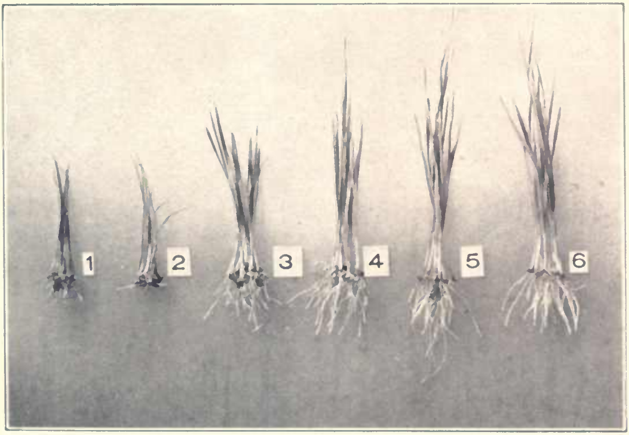

FIG. 2.—WHEAT SEEDLINGS GROWN IN EXTRACT OBTAINED IN THE METHOD FOR ISOLATING DIHYDROXYSTEARIC ACID FROM SOILS.

[1 and 2, undiluted extract; 3 and 4, one part extract, one part distilled water; 5 and 6, one part extract, nine parts distilled water.]

ISOLATION OF A WAXLIKE BODY; AGROCERIC ACID.

When this soil is treated with hot 95 per cent alcohol and filtered while hot, there is obtained a greenish-brown extract, from which on cooling a yellowish microcrystalline precipitate separates. If the soil be treated with successive portions of hot alcohol until the extract is no longer colored, the extracts combined, concentrated to a smaller volume, and allowed to cool, this precipitate can be obtained in considerable quantity. Two hundred and fifty parts per million of this substance have been obtained from this soil in this way, equivalent to 1,000 pounds per acre-foot.

The precipitate so obtained was washed with cold alcohol, redissolved in hot alcohol, and on cooling from this solution it crystallized fairly free of color. Thus obtained this crystalline body is evidently a mixture, since the melting point is quite variable as influenced by variations in the method, such as the concentration of the original alcoholic extract, extent of washing, etc. This variation in melting point extends from 70° to 90° C. If this mixture be thoroughly dried and washed with cold ether it is separated into two portions. The ether-soluble portion crystallizes on evaporation of the ether in minute leaflets which melt at 72° to 73° C. and solidify after melting at 67° C. It is little soluble in cold alcohol, readily in hot, the solution so obtained being acid to litmus. It separates from alcoholic solution on cooling in a powdery microcrystalline form.

On adding an alcoholic solution of lead acetate to the solution of this body in hot alcohol a precipitate containing lead is formed which after washing with cold alcohol and drying melts at 109° to 110° C.

The physical and chemical properties of this compound place it among the fatty acids found either free or combined in waxes both of vegetable and animal origin.

Elementary analysis gave the following figures:

	No. 1.	No. 2.
Carbon	73.2	73.40
Hydrogen	12.2	12.19
Oxygen	14.6	14.51

The only compound which corresponds with this percentage composition is that of a hypothetical acid, the lactone of which was found and described by Strucke[a] in carnauba wax.

This acid, $C_{21}H_{42}O_3$, would have the composition—

	Per cent.
Carbon	73.7
Hydrogen	12.3
Oxygen	14.0

and the figures obtained for the compound from the soil agree with these within the limits of experimental error.

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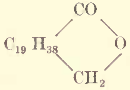
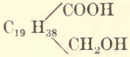
[a] Ann. Chem., **223**, 312 (1884).

Strucke isolated from carnauba wax and described a body to which he ascribed the formula



the lactone of an acid



which is the one referred to above and which has not been described or isolated. Whether this compound isolated from the soil is the same as the acid corresponding to the lactone isolated from the carnauba wax can only be determined by further investigation. The compound from the soil, which will be designated as agroceric acid, is almost insoluble in water and does not impart any harmful properties to distilled water when wheat seedlings are grown, although it is not impossible that other plants may be affected differently.

PRESENCE OF OTHER WAXLIKE BODIES.

The portion of the original precipitate from the alcohol extract insoluble in cold ether is evidently a mixture of bodies. The melting point of this mixture varies from 100° to 110° C. and it contains from 3 to 7 per cent of ash, mostly alumina. Elementary analyses corrected for ash have given carbon, 74 to 77 per cent; hydrogen, 12 to 13 per cent. It is evident from its physical properties and composition that this body is a mixture of higher acids, salts of such acids, and probably higher alcohols such as make up natural waxes. This mixture, like the ether-soluble portion, is almost insoluble in water and does not form a solution harmful to wheat seedlings.

ISOLATION OF A COMPOUND OF THE CHOLESTEROL GROUP; AGROSTEROL.

When the hot alcoholic extract of the soil obtained as described above is concentrated, cooled, and separated from the precipitate of agroceric acid and other compounds the filtrate is a dark greenish-brown solution which on evaporation leaves a thick, somewhat resinous material. On washing this residue with cold ether there is left a yellowish waxlike body, the nature of which has not been investigated. The ether solution, which carries with it nearly all of the color of the original extract, on spontaneous evaporation of the ether leaves a resinous material similar to that obtained from the alcoholic solution. On treating this residue with cold absolute alcohol the coloring matter goes into solution and there is left a nearly white microcrystalline substance. This body melts at 237° C. and the melting point remains constant after recrystallizing from alcohol, ether, and chloroform. It crystallizes from ether in fine needles arranged in radiating clusters, from alcohol, if a little water is present, in very thin plates of characteristic appearance, very similar to those of phytosterol. These crystals are shown in the photomicrograph in Plate III, figure 1. The compound is almost insoluble in water; difficultly soluble in cold alcohol, readily in hot, and readily soluble in ether and chloroform. It is unchanged on heating with alcoholic potash and can be obtained from the residue of the original alcoholic extract of the soil by treating this residue with alcoholic potash, evaporating to dryness, and extracting the dry residue with ether. The crystalline appearance and general properties of this body suggest a higher alcohol of the cholesterol group.

The color reactions ordinarily used to identify and distinguish members of this group when applied to this body gave the following results: Liebermann's "cholesterol reaction," which is the only one giving positive results with all the more commonly known members of the cholesterol group, gives the characteristic violet color with the compound obtained from the soil. This reaction consists in dissolving the substance in a small amount of chloroform, adding acetic anhydride, and then a drop of strong sulphuric acid, when a violet color is produced.

The other reactions ordinarily used in distinguishing compounds of this group gave no results with the soil compound. For instance, cholesterol when dissolved in chloroform and shaken with an equal volume of sulphuric acid (sp. gr. 1.76) gives a blood-red coloration in the chloroform layer. With the soil compound the coloration was light yellow. Again, when cholesterol is evaporated with strong hydrochloric acid containing 10 per cent of ferric chloride a violet-colored residue is left. With the soil compound no coloration is produced.

There have been quite a number of compounds described and named which seem to belong to this group of cyclic alcohols known as the cholesterol group and placed by Beilstein under the general formula $C_nH_{2n-8}O$. Most of these bodies are optically active and are found in fats and waxes, either free or combined. The combination is frequently one with fatty acids, the cholesterol in this case playing the same part that glycerol does in glycerides; cholesterol, however, and others of the group so far as known having only one alcohol or hydroxyl group.

Knowledge of the chemistry of this group is rather meager, cholesterol itself being the best known.

The compounds which have been described and placed in this group, together with their sources and some of their properties, are as follows: Cholesterol, $C_{26}H_{44}O+H_2O$, found in animal fats and in olive oil, melts at 148° C. Phytosterol, $C_{26}H_{44}O+H_2O$ "vegetable cholesterol," found in vegetable fats and waxes, melts at 132° C.

Isocholesterol, $C_{26}H_{44}O$, found in some animal fats, melts at 137° C., does not react with chloroform and sulphuric acid. Sitosterol, $C_{27}H_{44}O+H_2O$, in plant fats, melts at 137.5° C. Paraphytosterol, $C_{24}H_{40}O+H_2O$, in the seed coat of *Phaseolus vulgaris*, melting at 149° to 150° C. Paracholesterol, $C_{26}H_{44}O+H_2O$, found in slime mold, melts at 134° C. Caulosterol, found in etiolated yellow lupines, melts at 158° to 159° C. Parasitosterol, $C_{27}H_{44}O$, found in the embryo of wheat, melts at 127.5° C. Homocholesterol, $C_{28}H_{48}O$, found in Dalmatian insect powder (*Chrysanthemum cinerariæfolium*), melts at 183° C. Ergosterol, $C_{26}H_{40}O+H_2O$, found in ergot, melts at 154° C. Anthesterol, $C_{28}H_{48}O$, found in *Anthemis nobilis*, melts at 221° to 223° C. Arnesterol, $C_{28}H_{46}O$, in *Arnica montana*, melts at 249° to 250° C. Many of these bodies have as yet very doubtful standing as definite organic compounds, and much investigation will yet be necessary before the standing of these less-known bodies is assured, or the relationship between them is understood.

The composition of the compound obtained from the soil was found to agree very closely with the formula $C_{26}H_{44}O$. The analysis was made with material dried at 100° C. and was as follows:

	Found.	Calculated for $C_{26}H_{44}O$.
Carbon	83.6	83.8
Hydrogen	11.5	11.8
Oxygen	4.9	4.4

In the compound isolated from the soil, as described above, we have, no doubt, a member of the cholesterol group. Its method of preparation, physical and chemical properties, so far as ascertained, crystalline appearance, and the cholesterol reaction are all evidence of this, and point to the existence in the soil of a compound of the cholesterol group. The cholesterol substance obtained from the soil does not correspond in melting point with any substance of this group so far described. For this compound, isolated from a soil, having the chemical properties and general appearance of substances of the cholesterol group, but differing in melting point from any of the members of this group so far described, the generic name *agrosterol* is suggested in harmony with the nomenclature of this group.

With regard to the origin of this compound in the soil, at least two possibilities present themselves: It will be seen that several members of the cholesterol group are so far as known found only in single species of plants. It may be that agrosterol is characteristic of some plant grown on this soil, and that on the decay of plants of this species it has survived the action of enzymes, fungi, and bacteria and remained in the soil as an unchanged plant residue. Since, however, the presence of a substance of this group is shown by Liebermann's reaction above mentioned in several soils from widely separated localities with different native vegetation and cropping, it would seem that this suggestion has not much weight. To make this conclusive it would be necessary to show that the substances from different soils giving Liebermann's reaction are really identical, since the reaction is only a class reaction and not specific for agrosterol or any other member of the cholesterol group.

On the other hand, it is within the range of possibility that agrosterol may be formed from some other substance through the agency of micro-organisms or chemical oxidation. The fact that Lifschütz [a] has shown that a cholesterol substance can be formed by the oxidation of oleic acid emphasizes this possibility. The fact that paracholesterol mentioned above is found in slime molds further supports the suggestion that agrosterol may be formed by micro-organisms.

CULTURE TESTS WITH THE ISOLATED COMPOUNDS.

In the study of soil fertility from the point of view stated in the first part of this paper, the first and immediate interest concerning any organic compound isolated from or proven present in a soil is with regard to the possible effect of such compound on plants. While it is probably true that every organic compound in the soil which is at all soluble is to some extent a factor influencing plant growth either favorably or unfavorably, and that before there can be any true science of agricultural chemistry the chemistry of the organic soil material, harmless as well as injurious, must be known, it is evident that at this stage the interest of the investigator, as well as of the practical agriculturist, centers around the injurious organic soil compounds. Once the identity of a soil compound is established, it can usually be prepared artificially in quantity sufficient for an extended study of its effects on plants, both alone and as modified by other soil compounds or added chemicals, fertilizers, etc., an investigation which can not but furnish much of scientific interest and practical value.

Anything like the complete knowledge of the organic matter of soils or even one soil can be arrived at only after long research, research in a field as yet almost unknown and one presenting many difficulties incident to ignorance of matter under investigation and inadequacy of available methods. Such research will follow as the natural result of the demonstration of the presence of inhibiting organic compounds in soils in the most positive and practical manner by isolating such bodies so that they can be seen, handled, and experimented with.

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[a] Zeitsch. physiol. Chem., **55**, 1 (1908).

In determining the properties of bodies isolated from soils, wheat seedlings have been used as an indicator in the manner described in former bulletins.[a] While wheat seedlings only have been used in these tests, it is not impossible that other plants may show inhibited growth where the wheat is unaffected, and vice versa, as was found to be the case in the experiment with plant succession already mentioned, in which harmful effects were noted when wheat followed wheat or oats, but wheat following corn or cowpeas was either unaffected or else benefited. In carrying out the tests, wheat seedlings three or four days old of uniform size were grown in solutions of the substances tested, control cultures of similar seedlings in pure distilled water being carried on at the same time. The transpiration and green weight of plants at the end of the period of growth, generally ten or twelve days, together with observations made from day to day on the appearance of the roots and tops furnished the data from which the conclusion as to inhibition was drawn.

EFFECT OF PICOLINE CARBOXYLIC ACID AND RELATED COMPOUNDS.

The method by which picoline carboxylic acid was isolated from soils was essentially the precipitation of the acid as either the lead or silver salt from a neutral solution of a portion of the soil organic matter. The amount obtained from the soil by this method was very small. For this reason, and more particularly to meet the objection that any observed injury might be due to minute traces of lead or silver incident to the method of preparation, the effect of this compound was tested with the artifically prepared body. The method of preparing this, which has already been stated, is in outline the treatment of pyruvic acid in alcoholic solution with dry ammonia gas, precipitation of uvitonic acid with sulphuric acid and splitting of this into picoline carboxylic acid and carbon dioxide on heating. The yield, however, is small.

The following figures give the results obtained with wheat seedlings grown for ten days in solutions of different strengths of artificial picoline carboxylic acid.

Effect of picoline carboxylic acid on wheat seedlings.

Solutions.	Relative transpiration.	Relative green weight.
Control in distilled water	100	100
Picoline carboxylic acid, 1 p. p. m	140	95
Same, 10 p. p. m	105	101
Same, 50 p. p. m	107	98
Same, 100 p. p. m	85	89
Same, 200 p. p. m	55	70

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[a] Buls. Nos. 23, 28, 36, 40, 47, Bureau of Soils, U. S. Dept. Agr.

It is seen from the figures above, substantiated by the results of other series, that this soil constituent is harmful to wheat seedlings and in low concentrations is a stimulant, an effect which is, however, characteristic of small doses of poisons when applied to plants. In the solutions containing 100 and 200 parts per million in addition to the decreased transpiration and green weight of plants the roots showed the abnormal appearance characteristic of the presence of an injurious compound, little growth with root tips first darkened, then club-shaped, or hooked. However, since this body does not show marked injurious properties in solutions containing 50 parts per million and so far as can be determined occurs in the bad soil extract from the soil examined in less amount, it does not seem likely to explain by its presence the full effect of the injurious properties of the extract from the soil in which it was found. While this effect, as will be shown, is undoubtedly due to the presence of the more harmful dihydroxystearic acid in this particular soil, nevertheless it was thought to be of interest to study in this regard several bodies closely related to picoline carboxylic acid.

Uvitonic acid, from which picoline carboxylic acid is formed simply by heating to the melting point and which differs from it only by CO_2, is so closely related that it was thought desirable to test its effect even though there was no evidence of its presence in the soil. The result of such a test with wheat seedlings grown for twelve days in solutions of different strengths of uvitonic acid is shown by the following figures:

Effect of uvitonic acid on wheat seedlings.

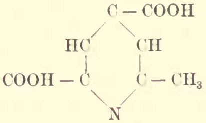
Solutions.	Relative transpiration.	Relative green weight.
Control in distilled water	100	100
Uvitonic acid, 1 p. p. m.	95	107
Same, 5 p. p. m.	88	116
Same, 10 p. p. m.	87	108
Same, 50 p. p. m.	39	78
Same, 100 p. p. m.	20	68
Same, 200 p. p. m.	35	Dead.

The plants growing in concentrations of 200 parts per million were dead when the test was terminated, and the transpiration of this set is higher, owing to this death of the plants, as dying plants frequently show increased transpiration.

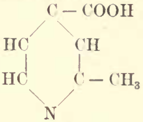
Uvitonic acid, it is evident, is quite harmful to wheat seedlings, much more so than the nearly related picoline carboxylic acid. It is also reported to be strongly antiseptic, which is again an indication of highly injurious properties for higher plants.

The relative effect of these two compounds brings up the question of the relation of chemical constitution to inhibitory effect on plant growth. Uvitonic acid and picoline carboxylic acid are related as shown by the structural formulas

Uvitonic acid.



Picoline carboxylic acid.



the former differing from the latter by CO_2, which on heating splits off from the carboxyl. Uvitonic acid, as shown, is a dicarboxylic acid, and the greater inhibition would seem to be associated with the presence of the second carboxyl group. However, all the carboxylic acids of pyridine and its homologues having one, two, and three carboxyls are weak acids. They form salts with bases in the usual way, but have also the power of forming salts with mineral acids by direct addition; for instance, the hydrochlorate, by the addition of hydrochloric acid. It is only in the higher members of this group, for instance, where all the H atoms are replaced by carboxyl, that the acid properties predominate and the power to form salts with mineral acids is lost. The whole question is one for future investigation, the data at present available furnishing little more than suggestions of possible explanations. It may be said, however, that the harmfulness of these compounds does not seem to be due to hydrogen ions.

Other related compounds, which may have a possible soil interest in this connection, have already been studied with the following results:[a]

Pyridine (C_5H_5N) forms the nucleus upon which are built many of the alkaloids. It is obtained chiefly from coal tar, but may also be obtained from a number of alkaloids, such as nicotine, trigonelline, sparteine, and cinchonine, when these are highly heated, treated with alkalies, or distilled with zinc dust. Pyridine is a colorless liquid of penetrating odor and basic properties. Laurent[b] found that a 1 per cent solution of pyridine was harmful to the fungi which he studied. It has been observed by Falkenburg[c] that the vapor of pyridine and some of its homologues is poisonous to bacteria.

In the experiments with wheat seedlings it was found that although pyridine, in a concentration of 1,000 parts per million, did not kill wheat plants in nine days it was nevertheless very injurious, especially to the growth of the green parts of the plants. In a concentration as low as 50 parts per million the growth of the tops was inhibited and the leaf tips turned brown. In the lower concentrations there was no stimulation of growth.

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[a] Bul. No. 47, Bureau of Soils, U. S. Dept. Agr., 1907.

[b] Ann. Soc. Belge Micr., **14**, 29 (1890).

[c] Czapek, Biochemie der Pflanzen, II, 926.

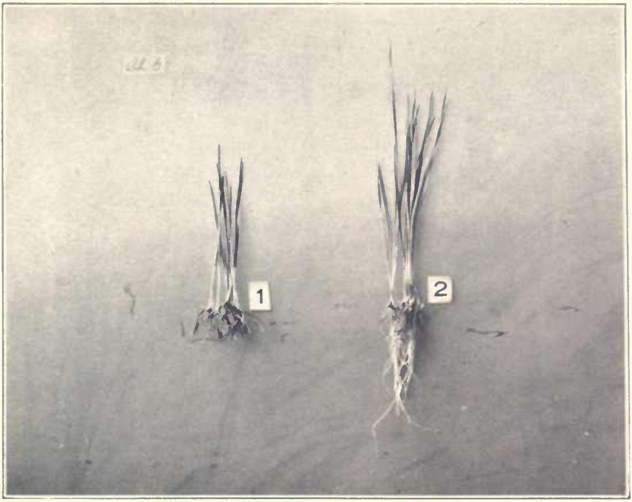

FIG. 1.—WHEAT SEEDLINGS SHOWING THE EFFECT OF DIHYDROXYSTEARIC ACID FROM SOILS.

[1, saturated solution of dihydroxystearic acid; 2, control in pure distilled water.]

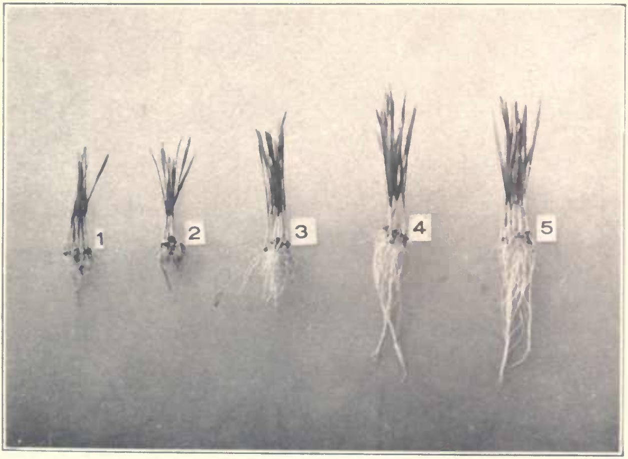

FIG. 2.—WHEAT SEEDLINGS GROWN IN SOLUTIONS OF DIHYDROXYSTEARIC ACID FROM SOILS.

[1, solution of dihydroxystearic acid, 200 parts per million; 2, 100 parts; 3, 50 parts; 4, 20 parts; 5, control in pure distilled water.]

Picoline ($C_5H_4N.CH_3$) or methyl pyridine was harmful to wheat plants, but only killed in the concentrations of 1,000 parts per million, and did not cause injury below 500 parts per million. The injury seemed to be manifested by the tops more than by the roots, thus resembling the action of pyridine.

Piperidine ($C_5H_{11}N$), or hexahydropyridine, is known to occur in nature, for example, in the pepper plant, and forms the nucleus of many alkaloids. Solutions of piperidine killed and injured at a lower concentration than either pyridine or picoline. A sample of piperidine that was neutralized with acetic acid proved to be more toxic than the strongly alkaline piperidine itself. Piperidine seems to injure the roots more severely than the tops.

Quinoline (C_9H_7N) has a genetic relationship with pyridine and forms the nucleus of many alkaloids found in plants belonging to the families Rubiaceæ and Loganiaceæ. Falkenburg[a] found that quinoline was harmful to bacteria in a concentration of 2,000 parts per million. Quinoline killed wheat plants at a concentration of 500 parts per million. So low a concentration as 5 parts per million affected them injuriously in six days. None of the lower concentrations caused stimulation of growth.

While picoline carboxylic acid may not be an important factor in the infertility of the Takoma soil, the fact that it has been found in other soils in larger quantities, its moderately harmful effect, and its close relationship to other pyridine compounds still more harmful, places it among organic soil compounds to be considered and sought for in the general study of unproductive soils.

EFFECT OF DIHYDROXYSTEARIC ACID.

The dihydroxystearic acid isolated from the soil was readily obtained in quantity sufficient for cultural experiments, and as its method of preparation was such that it could easily be obtained free of any reagents which might have an injurious effect, the body obtained from the soil was used in testing the effect of this compound. As a preliminary test a saturated solution of dihydroxystearic acid, which was found to contain approximately 200 parts per million at room temperature, was used as a culture solution for the growth of wheat seedlings. The result is shown in Plate IV, figure 1. Ten days' growth of the seedlings in this solution gave a green weight of plants 52.5 as compared with 100 for the same number of seedlings in distilled water for the same time. The water transpired by the plants growing in dihydroxystearic acid solution was 12.3 against 100 transpired by the plants growing in distilled water.

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[a] Czapek, Biochemie der Pflanzen, II, 926.

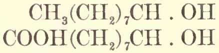
The harmful effect of this compound in not very high concentration being thus established, culture sets comprising several concentrations were then grown, the results of the ten days' growth being as follows:

Effect of dihydroxystearic acid on wheat seedlings.

Solutions.	Relative transpiration.	Relative green weight.
Dihydroxystearic acid 200 p. p. m	20	54
Same, 100 p. p. m	24	53
Same, 50 p. p. m	56	78
Same, 20 p. p. m	75	87
Control in pure distilled water	100	100

These results are illustrated in Plate IV, figure 2. The effect of this body, it will be noted, is as great in a concentration of 100 parts per million as in a concentration of 200 parts per million, which is approximately a saturated solution, and is marked even when the concentration is as low as 20 parts per million.

Artificial dihydroxystearic acid prepared as described from elaidic acid, as well as the isomeric dihydroxystearic acid formed on the oxidation of oleic acid, gave in concentration of 200 parts per million practically the same results, very little transpiration, green weight about half of that in the control solutions, and death of the plants in twelve or fifteen days. Other than this there has been no study of the effect of compounds related to the dihydroxystearic acid found in the soil.

Dihydroxystearic acid is, as may be inferred from its power to decompose carbonates, a much stronger acid than picoline carboxylic acid, and as represented by the formula  $\begin{matrix} CH_3(CH_2)_7CH\ .\ OH \\ COOH(CH_2)_7CH\ .\ OH \end{matrix}$ partakes also of an alcoholic nature. Whether the harmful effect of this compound is due to the combination of alcohol and acid characters, the so-called hydroxyacid structure, is of course not known. As has already been stated the whole question of the relation between effect on plant growth and composition and constitution is one which will be thoroughly understood only after long investigation. It may be well to note, however, in discussing the effect of a body of an acid constitution like dihydroxystearic acid that the data at present available is sufficient to prove that toxicity is not necessarily connected with the acid character or the presence of hydrogen ions. It is well known that an acid which is little dissociated in solution may be much more harmful than another which is dissociated to a much greater extent. For this as well as other reasons based on observations on the effect of organic compounds many of those who have studied this question hold that the harmful effect of organic compounds is in many cases associated with the structure of the molecule rather than due entirely to dissociation products.

Preliminary investigations have shown that some of the combinations of dihydroxystearic acid with bases are as harmful as the acid itself, although much less soluble. It was found that cultures in the calcium and potassium salts of dihydroxystearic acid gave greater green weights and greater transpiration than cultures in distilled water, while the iron and alumina salts, although less soluble than the acid, gave a growth and transpiration almost as low as solutions of the acid itself. The iron and alumina salts, because the least soluble, are perhaps the ones most likely to be present in soils. It would seem, then, that the injurious effect of this body when found in the soil may not be confined to that produced slowly during its formation, but that it may be stored up in a little-soluble but very harmful form.

SUMMARY.

Previous investigations have indicated that soils may be infertile or "exhausted" because of the presence in them of organic compounds injurious to plants.

The present paper deals with the isolation and identification of some of the inhibitory or injurious compounds in such infertile soils. It is almost self-evident that where such bodies give rise to infertile soils there can be intelligent scientific treatment of such soils only when the nature and properties of these bodies are known. The isolation and identification of these bodies is the first step in the attainment of this knowledge.

In approaching this problem, which is an exceedingly complex one, it was found necessary to review briefly the knowledge of the origin of the organic matter in the soil. This review shows that the soil organic matter arises through the decay of organic compounds of vegetable and animal origin; that among these compounds are many of well-known composition and constitution which get into the soil and may even persist for a time, and that many compounds which are formed from these in the process of decay are likewise well established as definite chemical compounds.

When the effect of these compounds which are known to get into the soil or to be formed in the soil is considered, it is found that many of them have been shown to be harmful to plants, some even when in very small amounts. On the other hand, it is not yet possible to trace any general relation between the harmful properties and the chemical composition or constitution, and consequently it is not possible to determine the effect of any compound on plants except by experiment.

In addition to known products of vegetable and animal origin and their products of decay, it is possible that still other compounds are produced and exist in the soil about which there is no knowledge, not even of a speculative kind. In view of these facts, it was found necessary to consider briefly the present knowledge of soil organic matter in general. It was found that although the organic matter in soils is an important ingredient, amounting in most cases to many tons per acre, almost nothing is known of the chemical nature of this material.

The difficulties, then, in attempting to isolate harmful organic compounds from infertile soils are due to ignorance of what compounds are harmful to plants and what are not, and also to lack of knowledge of the chemical nature of the organic matter of the soil and consequent lack of methods for dealing with such material.

The first crystalline organic compound isolated from a soil was a nitrogenous body, picoline carboxylic acid, which was obtained by a process which had its starting point in a solution of a portion of the organic matter in sodium hydrate solution. This body is a definite crystalline compound with very faint acid properties and has also the power of acting as a base toward strong acids. Along with the isolation of this compound there were obtained indications of the presence in the same soil of other bodies, some of which are related to it.

From the same and another soil by a modification of the same method another organic compound was obtained. This compound, dihydroxystearic acid, is nonnitrogenous and is in no way related to the nitrogenous body first isolated. Dihydroxystearic acid, like picoline carboxylic acid, is a well-defined crystalline chemical compound heretofore known only as a laboratory product.

The properties of these two organic compounds were tested by the effect of their solutions on wheat seedlings. Picoline carboxylic acid was found to be harmful in concentrations of 100 parts per million, and like many poisons had a stimulating effect when present in small quantities. Dihydroxystearic acid was injurious in all concentrations tested and ultimately caused death of the plants in concentrations of 100 parts per million.

Two other crystalline organic compounds previously undescribed in the literature were isolated from a soil. One of these, which has been named agroceric acid, is a member of the waxy acids; the other, which has been named agrosterol, belongs to the cholesterol group of bodies. Neither of these substances appear to be harmful to wheat and are of interest in the study of soil fertility chiefly with regard to their possible connection with the generation or destruction of injurious or beneficial compounds, although it is not impossible that they may be themselves harmful to plants other than that tested.

Apart from the purely scientific interest attached to the isolation from soil of any definite organic compound, the work here stated furnishes a simple tangible proof of the presence of injurious organic compounds in soils and should lay the foundation of the rational study and remedy of unfavorable conditions in such unproductive or so-called "exhausted" soils.

In the present bulletin there are described four organic compounds isolated from soils, all well-defined crystalline bodies, one of which is quite injurious, one slightly harmful but related to much more harmful compounds, and two that are not harmful so far as the wheat seedlings used in the tests are concerned, although, as pointed out above, other plants may be quite differently affected by these substances.

In addition to these, there have been isolated a number of other well-defined bodies, likewise crystalline. These various soil compounds are being studied and as far as possible their nature and properties will be determined and the results given in future publications.

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Issued December 31, 1908.

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U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF SOILS—BULLETIN No. 54.

MILTON WHITNEY, Chief.

THE MINERAL COMPOSITION OF SOIL PARTICLES.

BY

G. H. FAILYER, J. G. SMITH, AND H. R. WADE.

WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1908.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., July 23, 1908.

Sir: I have the honor to transmit the manuscript of an article entitled The Mineral Composition of Soil Particles, by G. H. Failyer, J. G. Smith, and H. R. Wade, and to recommend that it be published as Bulletin No. 54 of the Bureau of Soils.

Very respectfully.

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

PREFACE.

It is now generally understood that the mineral components of soils fall into two general classes. The first class comprises the common rock-forming minerals. It is generally the case, however, that a soil appears to be much more complex and to contain many more different minerals than any given rock. This is due in part to the fact that in the rock a certain few minerals which characterize that particular rock predominate to such an extent as to mask the other minerals which may be present. It is also due in part to the fact that the transportation of soil material from point to point, often to great distances, by wind and water and other agencies, produces a very complex mineral mixture, so that in almost any soil all or nearly all of the common rock-forming minerals can be found. It is very probable also that many minerals form in the soil. The various mineral fragments can be found to a greater or less extent through all the various sized soil particles, but in general, as might be anticipated from their origin, the finer the particles of the soil the more complex is the mineral mixture.

The second class of mineral components in the soil consists of decomposition products derived from the first class by the action of water and other weathering agencies of one kind or another. It is common knowledge that of these substances the silica, as quartz, tends to accumulate in the coarser grades of soil particles and ferruginous material in the finer grades. The distribution of the other products is not so obvious, although of the first importance for both theoretical and practical handling of soil problems.

The existing literature on this subject is meager and unsatisfactory. The tedious and difficult analytical operations involved have undoubtedly deterred investigators hitherto; but the importance of the subject in itself and as a connecting link in the larger problem of the mineral chemistry of the soil, which is being investigated by this Bureau, has led Mr. Failyer, with Messrs. Smith and Wade, to study the chemical composition of the soil separates of a number of soils, covering all the important agricultural areas of the United States. The mineralogical composition of these same separates is still under investigation.

The conclusions summarized at the end of the present bulletin may be taken safely as applying to soils generally, and mark another positive step forward in our knowledge of soils.

FRANK K. CAMERON.

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THE MINERAL COMPOSITION OF SOIL PARTICLES.

INTRODUCTION.

As is well known, soils are made up of mineral particles of many different sizes, and the relative proportions of the different sized particles have a most important influence on the physical properties of the soil and its adaptability to the growth of various kinds of crops. Therefore, in the mapping of soils by the Bureau, mechanical analyses of many type samples are made. By sedimentation, assisted by a centrifuge, soils are separated into arbitrary mechanical components called clay, silt, and sand. The latter is separated by sifting into five grades. As used by the Bureau, clay comprehends particles having a diameter of 0.005 mm. or less; silt includes particles whose diameters range from 0.005 to 0.05 mm.; very fine sand, particles from 0.05 to 0.1 mm.; fine sand 0.1 to 0.25 mm.; medium sand, 0.25 to 0.5 mm.; coarse sand, 0.5 to 1 mm.; very coarse sand, 1 to 2 mm.

It is a matter of interest and importance to know how these separates compare in their content of the important mineral plant-food constituents. For instance, whether phosphorus, potassium, and calcium be uniformly distributed through the sand, the silt, and the clay, or whether they be concentrated in one or more of these separates; and whether different classes and types of soils differ in this respect.

Another matter of interest is the influence of the manner of the formation of the soil and of climate upon the distribution of the several mineral nutrients. The past history of the soil greatly affects its mechanical and mineralogical composition. How it will affect the distribution of the plant-food constituents is not always obvious.

For some time investigators have recognized that the groups of various sized particles of a soil may differ in chemical composition. Considerable attention has been given to certain phases of the subject; but it has not as a whole received the detailed study that it deserves. Much of the analytical work that has been done upon the mechanical separates of soils has been by treatment with some conventional strength of hydrochloric acid. Such work is a study of solution and not of ultimate composition.

Apparently Loughridge[a] was the first to make any study of the chemical composition of the mechanical elements of a soil. By means of Hilgard's churn elutriator he prepared mechanical separates of a loam upland subsoil from Mississippi. The separates were extracted by five days' digestion in hydrocloric acid of 1.115 specific gravity and the solution analyzed. Larger proportions of potash, magnesia, iron, alumina, and silica were found in the extract of the finer portions than in that of the coarser. The lime was irregular and the soda and sulphuric acid somewhat uncertain.

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[a] Am. Jour. Sci., 7, 17 (1874).

Orth[a] made mechanical separations of samples of a soil taken at four depths. These samples consisted of the surface soil to a depth of about 8 inches—loamy sand; a layer of subsoil about 16 inches thick—loamy sand; a 16-inch layer of loam below the preceding, and a thick layer of marly loam under all of these. Chemical analyses, by decomposition with hydrofluoric acid, were made of each of these samples and of the particles of each under 0.01 mm. in diameter. The whole soil of each layer contained a greater percentage of silica than did the part less than 0.01 mm., while the latter contained a higher percentage of potash, lime, magnesia, soda, iron, alumina, and phosphoric acid. Orth does not make these comparisons, but a recalculation of his tabulated figures makes the comparison possible. It should be observed that this is not a direct comparison of the composition of the coarse with that of the fine particles. The whole soil is compared with its finest part. Indirectly, of course, a comparison is made of the coarser with the finer portions of this one soil and its subsoil.

Schneider[b] studied a residual soil from the Rockland Ridge, near The Dalles, on the Columbia River, Washington. The rock whose disintegration formed the soil is said to be an augite andesite, its principal constituents being "plagioclase, augite, apatite, magnetite, undifferentiated glass."

The soil was subjected to mechanical analysis by Hilgard's well-known method. For purposes of analysis, four groups were made of the sediments prepared from the fine earth—the part less than 0.6 mm. diameter. One group included particles of diameters between 0.5 and 0.1 mm.; another, particles between 0.1 and 0.01 mm.; another, those between 0.01 and 0.001 mm., and the last portion, particles less than 0.001 mm. This last fraction was called "clay."

Both fusion and acid digestion methods were used in analyzing these sediments, but as indicated in Table I, not all the analyses were carried to completion.

Table I gives Schneider's results calculated to water-free and organic-matter-free substance. The dimensions of the fractions are derived from Hilgard's "Table of diameters and hydraulic values of sediments."[c]

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[a] Ber., 15, 3028 (1882).

[b] Am. Jour. Sci., 36, 236 (1888).

[c] Am. Jour. Sci., 6, 337 (1873).

The author points out that the percentages of "alkalis and alkaline earths extracted by the hydrochloric acid decrease in the fractions almost proportionately to the decrease of total percentages obtained in the analysis by fusion."

From an inspection of Table I it is seen that the phosphoric acid and the magnesia are irregularly distributed among the sediments; that the lime decreases with the size of the particles; and that the potash, so far as given, increases as the particles decrease in size.

TABLE I.—*Partial composition of the separates of a soil analyzed by Schneider.*

Grade of material.	By fusion.			By acid digestion.			
	CaO	MgO	K_2O	P_2O_5	CaO	MgO	K_2O
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Particles 0.5 to 0.1 mm	6.57	2.60	1.54	0.14	3.02	1.06	0.32
Particles 0.1 to 0.01 mm	....	....	....	.18	2.60	.82	.38
Particles 0.01 to 0.001 mm	3.32	1.86	1.90	.46	2.23	1.56	.66
"Clay," less than 0.001 mm	.51	1.93	....	.14	.21	1.43	....

In studying the changes in composition when rocks weather to soils Merrill[a] has analyzed a soil and the "silt" separated from it. Under silt are included particles 0.1 mm. and less in diameter. This silt contained larger percentages of potash, lime, and magnesia than did the soil.

R. Sachsse[b] analyzed the fine earth of five soils and also the portions of these soils carried over by a stream of water of 0.2 mm. velocity. A comparison of the tabulated results shows great irregularity in the distribution of the elements. The lime, potash, and alumina are proportionately more abundant in the very fine particles than in the soil as a whole. The proportion of iron, magnesia, and soda is greater in the finer parts of some of the soils; in others the reverse is true. The phosphoric acid in the portions carried by the 0.2 mm. stream is not given. In this case, as before, the whole soil is compared with one of its parts.

Meyer[c] likewise compared the composition of the whole soil with that of its finer parts. Twenty-six soils differing much in physical character were used in his work. For analysis and comparison, three samples were prepared from each soil. One consisted of the whole soil, excluding gravel above 5 mm. in diameter. It was pulverized in a mortar to pass through a 0.5 mm. sieve, for treatment with acid as described below. Another sample was the "fine earth." It was obtained from a portion of the original soil by sifting, the part passing through a 0.24 mm. sieve being taken for analysis. The third sample was the clay or dust (staub). It was separated from another portion of the original soil by sifting, and consisted of particles not greater than 0.11 mm. in diameter. Since the finer grades of soil particles are found in all three samples thus prepared and the coarser ones are not, any differences in composition of the samples must be due to differences between the fine and the coarse particles. These samples were digested in hydrochloric acid for three hours at 100° C. and the extract analyzed. With very few exceptions he found greater percentages of lime, magnesia, iron and alumina, and phosphoric and sulphuric acids, in the extracts of the " fine earth " than in those of the whole soil, and greater percentages of these substances in the extracts of the " dust " than in those of the " fine earth." No determinations were made of the potash in the samples. Since only the substances dissolved by the acid were determined, this is more a solubility study than one of composition.

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[a] Bul. Geol. Soc. Am., **6**, 323 (1895).

[b] Chem. Centr.-Blatt., **66**, **1**, 752 (1895). The original publication (Geologische Spezialkarte der Königreichs Sachsen, Sektion Lommatzsch-Leuben) is not accessible to us.

[c] Landw. Jahrb., **29**, 913 (1900).

Tolman,[a] working on two soils from the arid region, found a greater degree of solubility in the finer particles, but the acid (hydrocholric acid of 1.115 sp. gr.) extracted notable amounts from all of the separates, even those of 2 mm. diameter. A higher percentage of potash, soda, magnesia, iron, alumina, and phosphoric acid was found in the solutions of the finer portions. The lime varied, but was an approximately constant constituent of the separates. He compared his results with those obtained by Loughridge and found, as might be anticipated, that much greater proportions of the soluble substances occur in the coarser grains of the arid soils than in those of like size in the humid soil.

Headden,[b] working upon a granitic soil on the station grounds, took a sample 10 inches deep and separated the fine earth (the portion passing through a sieve of 1 millimeter mesh) by beaker elutriation into 6 components. Complete chemical analyses were made of the " fine sand," particles 0.25 to 0.05 mm. in diameter, the " silt," 0.05 to 0.01 mm., the " dust," 0.01 to 0.001 mm., and the " clay," less than 0.001 mm. It is pointed out that the separates differ decidedly in composition, and that " there is an accumulation of potash in the finer portions of the soil, and a diminution of the silicic acid."

Westermann[c] investigated the relations of the " clay " (ler) content of certain Danish soils to their content of the several plant food constituents. He made mechanical analyses of 100 soils from eighteen counties well distributed over Denmark. Eighteen of these soils, varying in clay content from high to low, were digested forty-eight hours at 19° C. in 30 per cent hydrochloric acid, and the solutions analyzed. He finds no constant relation between the content of phosphoric or sulphuric acids extracted and of "clay;" the relation between the content of potash and of "clay" is close; there is a general similarity in the content of "clay" and of lime, magnesia, and iron, but there are important individual departures from the rule.

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[a] Rept. Cal. Agr. Expt. Sta., 1898–1901, Part I, p. 33.

[b] Bul. **65**, Colo, Agr. Exp. Sta. (1901), p. 19.

[c] Underslogelser over Typer af daniske Jorder, Copenhagen, 1902.

Bagger[a] studied the relation of the soluble potash content of soils to the impalpable matter they contain, using results of other workers as well as some of his own. In some of the published results of analyses he finds that soils containing the more clayey substances are richer in soluble potash; in others the reverse is true. Bagger himself examined eight soils of known history. A micaceous sandy soil containing little "clay" (abgeschlammte teile) was rich in potash soluble in concentrated hydrochloric acid, while heavy loams contained much "clay" and little potash. His general conclusion from his study of soils is that the potash content of the soil bears no definite relation to its mechanical composition, thus combating a view held by several agricultural writers. Potash is the only constituent considered by this author. He compares the potash extracted from the soils as a whole with that from the finer particles, and does not determine the potash in the mechanical separates themselves.

Schloesing[b] selected four soils that varied from very sandy to very clayey, and separated these into their mechanical components by a method of sedimentation, which is given. These separates were boiled with hydrochloric acid and the iron and phosphoric acid in the extracts determined. In each of the soils the iron and the phosphoric acid increased as the size of the physical elements decreased. The iron and the phosphoric acid contained in the undissolved mineral grains would not be determined by this treatment. Schloesing[c] also compares the separates of two subsoils as to their content of carbon. The soils above the subsoils are rich in organic matter. One of the subsoils is highly calcareous, the other nearly free from lime. Schloesing found that the finer portions of these subsoils are the richer in carbon. He is of the opinion that soil grains are coated with the various substances that have gone into solution in soils and have separated out again. Since the surface of small particles is greater compared to their mass than is the case with larger ones, these coatings would form a higher percentage of the finer separates, even if they be of the same thickness.

Rudzinski,[d] in the course of experiments in the growth of plants in the mechanical elements of soils, prepared separates of a clayey chernozem (black earth), a peaty clay, and a podzol soil (an ashy soil composed largely of very fine sand). He concludes from his chemical examination of the separates that the content of potash and of phosphoric acid in the mechanical elements of the soils investigated decrease with the increase of their size, and that the like separates from soils of like geological origin even are unlike in their chemical composition.

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[a] Inaug. Diss., Albertus-Universitat, Königsberg, 1902.

[b] Compt. rend., **134**, 631 (1902).

[c] Compt. rend., **135**, 601 (1902).

[d] Izv. Moscow Selsk. Khoz. Inst. (Ann. Inst. Agron., Moscow.), IX, No. 2, p. 172 (1903). (Expt. Sta. Rec. XVI, 345, 1904.)

Mazurenko[a] made mechanical analyses of two strikingly different soils, a loess and a podzol. The data show that in the separates of both soils the silica decreased and the other elements increased as the size of the particles decreased.

Dumont[b] compares the distribution of potash among the separates of two soils about equally rich in this substance, but very different as to origin and manner of formation. One was a fine-grained soil from an experimental field at Grignon, the other a coarse, sandy granitic soil from Creuse. They were separated into different sized particles by the method of Schloesing, the separates decomposed by hydrofluoric acid, and analyzed by usual methods.

Table II shows the percentage of potash in the separates, the potash of each separate expressed as percentage of the whole soil, and the percentage distribution of the potash of the soil among the separates.

Table II.—*Potash content of soil separates according to Dumont.*

Grade of particles.	Potash, per cent of separate.		Potash, per cent of soil.		Per cent of potash of soil in separate.	
	Soil of Grignon.	Soil of Creuse.	Soil of Grignon.	Soil of Creuse.	Soil of Grignon.	Soil of Creuse.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Coarse sand	0.864	1.33	0.148	0.605	16.55	70.93
Fine sand	.992	.58	.588	.225	65.78	26.37
Clay	.940	.51	.158	.023	17.67	2.70
	....	....	.894	.853	....	....

It is obvious that although these soils contain about the same proportion of potassium, the element is very differently distributed in their mechanical components. The separates of the Grignon soils are about equally rich in potash, while the sand of the soil of Creuse is nearly three times as rich as the clay. As pointed out by Dumont, five-sixths of the total potash of one soil is contained in its finer particles, whereas in the other, on the contrary, seven-tenths of the potash of the soil is in the coarse sand.

Hall[c] prepared separates of the Rothamsted soils by sedimentation. Composites were prepared by mixing the sediments of like grade derived from the several soils. The partial composition of these mixed sediments, as given by Hall, shows that the percentage of silica decreases and that of the alumina and the iron increases as the size of the sediments decreases—an observation confirmed by work in this laboratory for soils in general.

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[a] Inaug. Diss., Munich; Abs. in Zhur. Opuitn. Agron. (Jour. Expt. Landw.), V, No. 1, p. 73 (1904). (Expt. Sta. Rec. XVI, 344, 1904.)

[b] Compt. rend., **138**, 215 (1904).

[c] Jour. Chem. Soc., **85**, 950 (1904).

Puchner,[a] in an article on the distribution of nutrients in the separates of the soil, describes his work upon three soils differing widely in physical character and in geological origin.

Soil No. 1 was a heavy loam; No. 2, a silty soil (loessial); No. 3, a coarse sandy soil from gneiss. These soils were resolved into their mechanical components, four divisions being made of the particles less than 0.25 mm. in diameter. Complete analyses were made of these finer separates. The medium and coarse sands not being analyzed, no comparison of the composition of these with the finer portions can be made.

The composition of the finer separates of the three soils is given in Table III. Table IV gives the content of the elements in the several separates calculated to percentages of the soil.

TABLE III.—*Composition of the mechanical separates analyzed by Puchner.*

[The figures express percentages of the separates.]

Mineral constituent.	1. Heavy loam.				2. Loamy loess soil.				3. Coarse sandy gneiss soil.			
	Coarse dust, 0.25 to 0.01 mm.	Medium dust, 0.01 to 0.005 mm.	Fine dust, 0.005 to 0.0015 mm.	"Clay" (Schlamm) 0.0015 to 0 mm.	Coarse dust, 0.25 to 0.01 mm.	Medium dust, 0.01 to 0.005 mm.	Fine dust, 0.005 to 0.0015 mm.	"Clay" (Schlamm) 0.0015 to 0 mm.	Coarse dust, 0.25 to 0.01 mm.	Medium dust, 0.01 to 0.005 mm.	Fine dust, 0.005 to 0.0015 mm.	"Clay" (Schlamm) 0.0015 to 0 mm.
CaO	Tr.	Tr.	0.04	Tr.	7.23	6.28	4.09	3.39	2.55	1.18	2.23	2.44
MgO	0.39	1.42	1.08	0.15	2.41	2.08	1.45	1.19	0.31	.42	.81	.32
K_2O	4.14	1.02	.12	.01	.81	.70	.67	.56	.08	.05	.04	.06
Na_2O	2.35	2.29	2.01	1.18	3.25	3.05	3.02	2.48	3.05	2.94	1.43	1.22
Fe_2O_3	2.49	5.14	8.95	12.50	3.77	4.98	6.86	9.85	5.38	7.20	9.23	11.11
Al_2O_3	4.63	15.20	20.48	27.76	7.28	14.20	19.41	29.97	18.71	24.20	30.21	32.42
Mn_3O_4	Tr.	.70	1.10	3.65	1.54	1.88	1.94	2.79	1.56	1.74	2.48	3.10
P_2O_5	.03	.08	.08	.19	.15	.12	.17	.03	.06	.03	.05	.04
SiO_2	87.51	72.08	63.22	51.01	71.45	63.95	59.40	50.23	58.00	61.70	52.22	46.54
Humus	.74	1.48	2.00	3.32	.11	.76	.89	1.97	.23	.59	1.40	2.81

TABLE IV.—*The P_2O_5, CaO, MgO, and K_2O, in the separates analyzed by Puchner, calculated to percentages of the total soil.*

Mineral constituent.	1. Heavy loam.				2. Loamy loess soil.				2. Coarse sandy gneiss soil.			
	Coarse dust, 0.25 to 0.01 mm.	Medium dust, 0.01 to 0.005 mm.	Fine dust, 0.005 to 0.0015 mm.	"Clay" (Schlamm) 0.0015 to 0 mm.	Coarse dust, 0.25 to 0.01 mm.	Medium dust, 0.01 to 0.005 mm.	Fine dust, 0.005 to 0.0015 mm.	"Clay" (Schlamm) 0.0015 to 0 mm.	Coarse dust, 0.25 to 0.01 mm.	Medium dust, 0.01 to 0.005 mm.	Fine dust, 0.005 to 0.0015 mm.	"Clay" (Schlamm) 0.0015 to 0 mm.
P_2O_5	0.02	0.03	Tr.	0.02	0.10	0.03	Tr.	Tr.	0.01	0.01	Tr.	Tr.
CaO	Tr.	Tr.	Tr.	Tr.	4.67	1.63	0.04	0.23	.43	.27	0.11	0.13
MgO	.20	.46	Tr.	.01	1.56	.54	.01	.08	.05	.10	.04	.02
K_2O	2.08	.33	Tr.	Tr.	.52	.18	.01	.04	.01	.01	Tr.	Tr.

[a] Landw. Vers.-Stat. 66, 463 (1907).

From the results Puchner draws the conclusion that as the mechanical separates become finer the content of silicic acid, soda, and potash diminishes. On the contrary, that of alumina, iron, manganese, and humus increases. The content of lime, magnesia, and phosphoric acid in the separates is irregular.

Alway and McDale[a] conclude from their study of the distribution of carbonates in the till of the second steppe of the northern Great Plains region that the carbonates are chiefly present in the grains of intermediate size; i. e., the silt particles running from 0.05 to 0.005 mm. in diameter.

Clerk, Gortner, and Vail,[b] working upon a sample of bowlder clay representing the upper 6 feet, made four mechanical fractions—sand, 1.0 to 0.05 mm.; coarse silt, 0.05 to 0.016 mm.; fine silt, 0.016 to 0.005 mm.; clay, smaller than 0.005 mm. These fractions were analyzed chemically by digestion in hydrochloric acid and the determination of the dissolved substances.

In this soil the lime, as carbonate for most part, formed the highest percentage in the silts and least in the clay; the iron, alumina, soda, potash, and phosphoric acid were in greater proportions in the finer fractions; the silts contained the highest percentage of magnesia and the clay the next.

In addition to the investigations mentioned above, numerous chemical and mechanical analyses of the same soil have been made. From the published results of this work one could make comparisons of the total percentages of the several chemical elements in a soil with its percentage content of any particular mechanical component. For example, it could be determined for each soil whether a high content of calcium goes with a high content of sand, of silt, or of clay; but since the investigators themselves did not study these relations, such purely physical and chemical analyses of soils have not been included in a historical review of the literature of the chemical composition of the mechanical separates of soils.

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[a] Am. Chem. Jour., **37**, 275 (1907).

[b] Am. Chem. Jour., **39**, 163 (1908).

NOTE.—Since the manuscript for this bulletin went to the printer a report of additional work along the line of this investigation has come to hand:

Atterberg (Landw. Vers.-Stat., 69, 102, 1908), working upon a glacial sand from Kulltorp, made complete analyses of the six groups into which he separated the portion between 0.5 mm. and 0.005 mm. diameter. In the table of results given by them the aluminum is a nearly constant constituent; there is an increase in the percentage of the iron and the calcium as the size of the particles decreases except in the finest portion—that between 0.01 and 0.005 mm.—in which these elements decrease. The potassium and the sodium decrease as the particles become smaller.

SELECTION OF SOIL SAMPLES.

Our extensive collection of soils from important and well-marked soil types enables us to select samples fully representative of the soils of the country. Accordingly, agricultural soils of known character were selected so as to include those from various geographical sections and from a number of soil provinces. Thus we have taken soils from the Coastal Plains, the Piedmont region, glacial soils, non-glaciated soils of the interior, and those of the arid region, the list comprising 27 soil types. These soil types are fully described in the reports of the Field Operations of the Bureau of Soils and in the Soil Survey Field Book, but since these publications may not be easily accessible to readers of this bulletin, the several types analyzed are described briefly in the proper place. The samples taken for analysis are from the surface soil, but the field characteristics of a type, as well as its agricultural value, are often largely dependent upon the subsoil. The subsoils, therefore, often serve to differentiate one soil type from another. The characteristics of the subsoil should therefore be considered an essential part of the description of a soil type. In view of these facts it is obvious that definite conclusions regarding the productiveness of a soil can not be made from a study of the surface soil alone.

Two hundred gram composite samples of the several soil types were separated into the three grades—sand, silt, and clay. In making these separations the whole of the water was poured into the clay dish and evaporated to dryness. Thus any material which dissolved in the repeated treatment of the soil with water was carried into the clay, and this fact must be considered in comparing the results of the analyses of the separates.

The important mineral nutrients only were determined; that is, phosphorus, potassium, calcium, and magnesium. A complete analysis of the soil separates, so far as these constituents are concerned, was made by fusion methods, so that the total content was obtained, and not simply that which would have been extracted by treatment with acid of some conventional concentration.

In the tables giving the results of the analyses the figures are the percentages of the respective substances in the ignited separates, and thus free from organic matter and water. The aim has been to learn the composition of the strictly mineral matter of the soils. It seems safe to assert, however, that were calculations made on the oven-dried soils there would merely be changes in percentages and no material ones in the order of these, so that conclusions based upon them would be consistent with those based upon the mineral matter, as here given.

SOILS OF THE COASTAL PLAINS.

The Coastal Plains are made up of unconsolidated gravels, sands, silts, and clays derived in most part from the erosion of the Piedmont Plateau and other inland areas. These materials were mainly deposited on the then ocean floor and have been brought to their present level by the elevation of the land areas.

The character of the soils of the Coastal Plains in a broad way, therefore, depends upon that of the rocks and soils of the Piedmont Plateau, but they are modified by deposits from other sources. Thus in the northern portions glacial material is mixed to some extent with the débris of the disintegrated and more or less decomposed rocks of the plateau. In some instances, streams which rise far inland and drain limestone regions have brought materials not common to most of the Coastal Plains soils. While the soils of this region present many diversities among themselves, due to special circumstances affecting their deposition or subsequent history, they all differ much from the parent rock and have been subjected to excessive weathering and leaching.

In studying soils and the results of their analyses, it should be fully recognized that the soil as now found is a distinct product or entity. Simple crushed rock represents no very important agricultural soil. Plants will grow in certain rock powders if compounds of nitrogen be present, but such a " soil " is nowhere found in extensive areas, except possibly as subsoils, and some subsoils were once real surface soils. Unconsolidated rock material should be called rock and not soil, unless it has been subjected to the processes called weathering, with all the numerous changes implied by the term, including those produced by high and low forms of animal and plant life. The soil depends primarily, in the sense of first cause, upon the rock or the rocks from which it originated. As a first step in soil making, the rocks may disintegrate or be crushed to sand or dust. Mechanical agencies may separate the pulverized rocks into groups according to size of particles and deposit them as beds of sand, silt, or clay; or these may remain together, giving rise to loams. Solution and hydration and other chemical processes may effect changes which in some cases leave many of the original mineral grains; in others, the changes may be so profound that few of the original minerals other than quartz remain. The latter extreme condition is less common than is generally supposed, the original minerals, though undoubtedly present, being in so finely divided a form as to be difficultly recognized. Absorptions taking place in soils and other facts make it probable that new minerals similar, if not identical, to those existing in rocks are formed in soils in minute particles. A soil will then be best understood when all the factors which have operated to produce it are known; that is, when the whole history of the formation of the soil is known. This must often be inferred from the present character of the soil and the geological history of the region. From these considerations it might be expected that soils formed in one general way, as the Coastal Plains soils have been, would constitute a class by themselves and differ in important particulars from those that have had an entirely different history, as glacial soils, for instance. This subject will be referred to again in comparing groups of soils after the analytical data have been given.

The Coastal Plains soils are mostly light: sands and light sandy loams predominating. Those selected for our work are the Collington sandy loam from New Jersey; Norfolk sand, Norfolk loam, and Leonardtown loam from Maryland: Orangeburg sandy loam from Alabama; Crowley silt loam from Louisiana; Orangeburg fine sandy loam from Texas.

Collington sandy loam.—The sample analyzed is from the Salem area, New Jersey, surveyed in 1901. The soil is a loose, coarse, sandy loam. It is of a brown color and frequently contains considerable amounts of gravel. It has resulted from the weathering of the greensand, or glauconite, of New Jersey. The subsoil, which comes within 6 or 8 inches of the surface, is a sticky, tenacious, claylike material, yellowish or greenish in color. Owing to its relations to the greensand deposits, this type differs from the other Coastal Plains soils.

Norfolk sand.—The sample of this type analyzed is from Prince George County, Md. The area was surveyed in 1900. This is a coarse to medium orange or yellow sand, having a depth of about 10 inches. The subsoil is coarse to medium, becoming loamy at about 3 feet. It is a common type of soil in the Atlantic and Gulf Coastal Plains. The surface is level to rolling and the soil is well drained.

Norfolk loam.—The soil is from the Worcester County area, Maryland, surveyed in 1903, and was mapped as Sassafras sandy loam. This soil is a mellow brown sandy loam to a depth of about 9 inches. The subsoil to 36 inches is a medium to heavy loam, which is often underlain by fine yellow sand. In the area from which the samples were taken it has a slight elevation and is gently rolling. It is usually well drained.

Leonardtown loam.—The samples used were collected in the soil survey of St. Mary County, Md., 1900. The soil of this type consists of a yellow silty loam, fine and powdery when dry, but puddling to a plastic mass when thoroughly wet. The subsoil consists of a brittle mass of interlocking clay lenses, lumps, and fragments, separated by seams and pockets of medium to fine sand. This subsoil is as impervious as clay, owing to its peculiar shinglelike structure. It is an upland soil and is generally slightly rolling.

Orangeburg sandy loam.—Samples analyzed are from Montgomery County, Ala., surveyed in 1905. This soil, locally called "red lands," is a brown to reddish-brown light sandy loam, 4 to 15 inches deep, resting on a friable brick-red sandy clay subsoil. The surface is rolling. It is generally well drained, although there is a tendency to form a "plowsole" or "hardpan."

Crowley silt loam.—The samples used were taken from samples of soil collected in the survey of Acadia Parish, La., 1903. This type is of variable depth, but usually has a surface soil of about 16 inches. It is of a brown color when wet, but ash gray when dry. It is composed of fine sand and silt, with sufficient clay to render it rather impervious. If stirred when wet it puddles somewhat. This soil is underlain by a clay of mottled brown and yellow color, with brick-red streaks and blotches. The subsoil is highly impervious and the surface level, so that the soil has very poor drainage. The samples analyzed are from level prairies in southern Louisiana.

Orangeburg fine sandy loam.—The samples used came from the Nacogdoches area, Texas, survey of 1903. This soil varies in color, being red, brown, or gray. It is a light sandy loam, generally carrying iron concretions. The subsoil is a red, friable, sandy clay. The type occupies the upland and has good natural drainage.

The percentage of the several mechanical constituents—sand, silt, and clay—contained in the soils is given in Table V. The results of the chemical analyses of the mechanical separates for phosphoric acid, lime, magnesia, and potash are given in Tables VI and VII. In Table VI the figures express percentages of the separates; in Table VII the percentages are calculated on the whole soil, so that the figures show what percentage the constituent in a separate is of the soil of which the separate is a part.

An inspection of Table VI shows that the elements determined—phosphorus, calcium, magnesium, and potassium—are more abundant in the finer particles of these old soils—old in the sense of having passed through and being the result of all the stages of soil formation.

As shown in Table VII, the coarse particles often contain absolutely more of the elements than the finer portions, but this, of course, is due to the presence in the soil of a much greater percentage of these large particles.

TABLE V.—*Mechanical composition of the Coastal Plains soils.*

Soil type and location.	2 to 0.05 mm. (sand).	0.05 to 0.005 mm. (silt).	0.005 to 0 mm. (clay).
	Per cent.	*Per cent.*	*Per cent.*
Collington sandy loam, New Jersey	78.5	14	6.5
Norfolk sand, Maryland	85.5	10	4
Norfolk loam, Maryland	64.5	25.5	9
Leonardtown loam, Maryland	29.5	55	15
Orangeburg sandy loam, Alabama	71	16	12
Crowley silt loam, Louisiana	15	59	26
Orangeburg fine sandy loam, Texas	69	22	9

TABLE VI.—*Partial chemical composition of the separates of the Coastal Plains soils.*

Soil type and location.	P_2O_5.			CaO.			MgO.			K_2O.		
	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Collington sandy loam, New Jersey	0.01	0.09	0.13	0.06	0.30	0.40	0.18	0.22	0.66	0.49	1.86	2.25
Norfolk sand, Maryland	.01	.10	.94	.07	.27	.98	.19	.11	.48	.33	2.38	2.35
Norfolk loam, Maryland	.01	.06	.42	.09	.23	1.30	.02	.19	.48	.44	1.49	1.39
Leonardtown loam, Maryland	.01	.02	.03	.04	.08	.13	.07	.25	.87	.56	1.20	1.88
Orangeburg sandy loam, Alabama	.01	.21	.21	.03	.19	.24	.01	.11	.14	.05	.96	1.48
Crowley silt loam, Louisiana	.08	.08	.32	.11	.16	.29	.09	.05	.97	.51	.80	1.47
Orangeburg fine sandy loam, Texas	.07	.12	.36	.10	.09	.54	.04	.06	.70	.21	.66	1.50

TABLE VII.—*The content of the separates of the Coastal Plains soils calculated on the whole soil.*

Soil type and location.	P_2O_5.			CaO.			MgO.			K_2O.		
	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay	Sand.	Silt.	Clay.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Collington sandy loam, New Jersey	0.01	0.01	0.01	0.05	0.04	0.03	0.06	0.03	0.04	0.38	0.26	0.15
Norfolk sand, Maryland	.01	.01	.04	.06	.03	.04	.16	.01	.02	.28	.23	.09
Norfolk loam, Maryland	.01	.02	.04	.06	.06	.12	.01	.05	.04	.28	.38	.13
Leonardtown loam, Maryland	.01	.01	.01	.01	.04	.02	.02	.14	.13	.17	.66	.28
Orangeburg sandy loam, Alabama	.01	.03	.02	.02	.03	.03	.01	.02	.02	.04	.07	.17
Crowley silt loam, Lousiana	.01	.05	.08	.02	.10	.07	.01	.03	.25	.07	.48	.37
Orangeburg fine sandy loam, Texas	.05	.03	.03	.07	.02	.05	.03	.01	.06	.14	.15	.13

SOILS FROM CRYSTALLINE AND METAMORPHIC ROCKS.

Three soils, not of glacial origin, formed from crystalline and metamorphic rocks, were selected for this work—Chester mica loam (Maryland), Porters black loam (Virginia), and Cecil clay (North Carolina.)

Chester mica loam.—Described as Cecil mica loam in the report of the Soil Survey of Harford County, Md., 1901. This soil, as its name indicates, is characterized by a great quantity of micaceous particles. It is derived from granites, gneisses, and other micaceous rocks over which the type lies. It is strictly a residual soil and consists of a brownish loam 10 to 15 inches deep, underlain by a lighter colored, heavier loam, also containing mica. The surface varies from gently rolling to somewhat hilly.

Porters black loam.—The sample analyzed was collected in the soil survey of the Albemarle area, Virginia, 1902. The soil of this type is a loose, mellow black loam, averaging about 12 inches deep. The subsoil is slightly heavier and of a light-brown to yellowish color. In depressions and coves, where wash from the higher ground has accumulated, there is no sharp distinction between soil and subsoil, the loose black loam being several feet deep. Both soil and subsoil contain fragments of the rocks whose decomposition has formed the soil—granites, gneisses, and schists. This type occurs principally in the coves of the Blue Ridge Mountains, but is also found upon the tops and upper slopes.

Cecil clay.—The samples of this type were collected near Statesville, N. C., in the survey of that area in 1901. This type is found on uplands, gentle slopes, and rolling lands of the Piedmont Plateau. The Cecil clay is a residual soil, resulting from the disintegration of a number of rocks, differing in mineralogical characters. Granites, gneisses, schists, and other somewhat similar rocks have contributed to the formation of this type, and so thorough have been the disintegration and decomposition that the same red clay results from all. There is such a gradual change from soil to the parent rock that there is generally no sharp line between the two. The soil consists of a heavy red loam, containing many sand grains of the original minerals forming the rocks from which the soil is derived. It is shallow, averaging about 5 inches. The subsoil is a stiff, tenacious red clay to a depth of 3 or more feet. It becomes heavier at greater depths. Natural drainage is fairly good, probably due to the sand and rock fragments contained in soil and subsoil.

The mechanical composition and the results of the analyses of the separates of these soils are given in Tables VIII, IX, and X.

With few exceptions the percentage of the several mineral plant-food constituents increases as the size of the particles of the separates decreases. Chester mica loam, however, which contains many micaceous scales, shows a nearly constant percentage content of lime and magnesia in its separates, while Cecil clay shows the reverse order as to the potash content, the sand being richest in potash, the silt slightly poorer, and the clay decidedly the poorest of the three. While there are some notable exceptions, the absolute quantities are generally fairly evenly distributed in the mechanical components of these soils, as shown in Table X.

TABLE VIII.—*Mechanical composition of the residual soils formed from crystalline and metamorphic rocks.*

Soil type and location.	2 to 0.05 mm. (sand).	0.05 to 0.005 mm. (silt).	0.005 to 0 mm. (clay).
	Per cent.	*Per cent.*	*Per cent.*
Chester mica loam, Maryland	36	83	30
Porters black loam, Virginia	53	23	24
Cecil clay, North Carolina	58	17	24

TABLE IX.—*Partial chemical composition of the separates of soils formed from crystalline and metamorphic rocks.*

Soil type and location.	P_2O_5.			CaO.			MgO.			K_2O.		
	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Chester mica loam, Maryland	0.04	0.06	0.33	0.22	0.24	0.28	0.96	0.81	0.88	1.44	2.56	2.55
Porters black loam, Virginia	.15	.53	1.36	1.20	2.07	2.30	.33	1.37	2.28	1.86	3.10	5.06
Cecil clay, North Carolina.	.03	.06	.32	.08	.15	.23	.16	.40	.55	1.49	1.45	.97

TABLE X.—*Content of the separates of residual soils from crystalline and metamorphic rocks, calculated on the whole soil.*

Soil type and location.	P_2O_5.			CaO.			MgO.			K_2O.		
	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Chester mica loam, Maryland	0.01	0.02	0.08	0.08	0.07	0.07	0.34	0.25	0.23	0.51	0.79	0.68
Porters black loam, Virginia	.08	.12	.33	.64	.47	.55	.17	.31	.55	.99	.70	1.21
Cecil clay, North Carolina.	.02	.01	.08	.05	.03	.06	.09	.07	.13	.87	.25	.24

SOILS OF GLACIAL ORIGIN.

The group of soils of glacial origin includes soils formed from material deposited by glaciers or this material somewhat reworked by water, and also loessial soils, consisting largely of particles the size of silt, which have been carried from other glacial areas and deposited over the underlying material. The transporting agents in this case were wind and water.

The mechanical composition is given in Table XI; the results of the chemical examination are given in Tables XII and XIII, calculated as before upon the separates and the soils, respectively.

Podunk fine sandy loam.—The sample for analysis was taken from a large sample from a very sandy phase of the type found in the Connecticut Valley. The area was surveyed in 1903. This is an alluvial soil, formed by the reworking by running water of glaciated granites, gneisses, and schists. It contains an abundance of micaceous mineral particles visible to the eye. It is underlain by fine sand. The soil is of a dark-brown color and is well drained. The tobacco field from which the sample came had been heavily fertilized for years.

Miami sand.—From the Toledo area, Ohio, surveyed in 1902. The soil is a coarse to medium loose and deep yellowish sand. It is underlain by a yellow sand of about the same texture. It is level to rolling and consists of glacial material somewhat modified by wind action. It occupies elevated positions and is well drained.

Wabash loam.—Described as Miami loam in the Report of the Soil Survey of the Toledo Area, Ohio, 1902. This is a dark-brown to black soil of good depth, and containing a small proportion of the coarser grades of sand. The subsoil is a heavy brownish-yellow loam overlying a fine gravelly loam. It is a bottom land, frequently occurring as terraces. It is generally well drained. It consists of glacial drift redeposited by stream action.

Volusia silt loam.—The sample for analysis was collected in the soil survey of the Wooster area, Ohio, 1904. This soil is a gray to brown silty loam with an average depth of 8 inches. The subsoil is a light-yellow silty loam, mottled with gray in its lower portions. It has resulted in most part from the glaciation of shales. Its mechanical constituents closely resemble in size those of the soils derived from the loess, being composed largely of silt. This is doubtless due to the silt in the shales from which this soil type comes in large part.

Marshall loam.—From samples of this type collected during the survey of the Marshall area, Minnesota, 1903. The surface soil is a somewhat heavy loam from 10 to 12 inches in depth and of a dark-brown color. Under this is a stiff, sticky yellow subsoil to a depth of about 3 feet. Below this is a stiff bowlder clay, mottled yellow and gray. The type is generally rolling and well drained. Bowlders and glacial gravel occur to some extent over this soil.

Miami silt loam.—Described as Edgerton silt loam in the Report of the Soil Survey of the Janesville Area, Wisconsin, 1902. The soil is a very silty loam, light brown when wet and light gray when dry. Its depth is about 8 inches. It is underlain by several feet of stiff, yellow, silty clay that is always mottled with gray, showing poor drainage and aeration. This type originally consisted mainly of timber lands and oak openings.

Marshall silt loam.—Described as Janesville silt loam in the Report of the Janesville Area, Wisconsin, 1902. The soil is a mealy, chocolate-colored silt loam with a dark-brown tint when moist. It contains a large amount of silt and becomes somewhat sticky when wet. It is about 10 inches deep. The subsoil is a sticky, reddish-yellow silty clay, about 3 feet deep, and rests upon a glacial gravel or the disintegrating limestone of the region. The soil probably owes some of its distinguishing characteristics to the influence of this limestone.

The type is rolling and well drained. It was originally covered with the prairie grasses of the region.

Marshall black clay loam.—Samples collected in the survey of McLean County, Ill., 1903. This soil is a heavy, somewhat sticky granular clay loam, containing a large percentage of silt and organic matter It has a depth of about 18 inches. The subsoil is a mottled yellow or drab-colored sticky, silty clay. This soil type has formed where the natural drainage was poor. The surface is level. In its original condition it was wet and swampy and required thorough drainage.

Marion silt loam.—Samples from Clay County, Ill. The area was surveyed in 1902. The Marion silt loam consists of a light-brown to whitish very silty loam, containing very little organic matter. Its depth averages 12 inches. The soil cakes on drying, but breaks down into flour-like dust when pulverized. The subsoil is heavier and contains more clay. It is so impervious to water as to be locally called hardpan. The lower subsoil is a hard, silty, mottled yellow clay, often containing iron concretions. Below 4 or 5 feet more or less glacial gravel is found. The type is level or slightly rolling. The soil has very poor natural drainage, owing to the rather impervious subsoil and the level surface. While of loessial origin, this soil has been largely formed from sandstones and shales ground up by glaciers.

Shelby silt loam.—The sample analyzed was collected in the soil survey of Shelby County, Mo., 1903. The Shelby silt loam is a silty soil of medium depth and of a light-gray color when dry; dark gray when wet. It grades into a stiff, impervious silty clay, plastic and waxy when wet, friable and loamy when dry. The subsoil is a dark mottled clay. It is level or gently rolling. The original growth on this type of soil was the prairie grasses.

TABLE XI.—*Mechanical composition of the glacial soils.*

Soil type and location.	2 to 0.05 mm. (sand).	0.05 to 0.005 mm. (silt).	0.005 to 0 mm. (clay).
	Per cent.	*Per cent.*	*Per cent.*
Podunk fine sandy loam, Connecticut	80.5	18	2
Miami sand, Ohio	91.5	5.5	3.5
Wabash loam, Ohio	50.5	38	12
Volusia silt loam, Ohio	17	64	19
Marshall loam, Minnesota	48	38	13
Miami silt loam, Wisconsin	14	72	14
Marshall silt loam, Wisconsin	12	70	17
Marshall black clay loam, Illinois	21.5	57.5	20
Marion silt loam, Illinois	13	69	18
Shelby silt loam, Missouri	7	74	19

TABLE XII.—*Partial chemical composition of separates of the glacial soils.*

Soil type and location.	P_2O_5.			CaO.			MgO.			K_2O.		
	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Podunk fine sandy loam, Connecticut	0.12	0.31	3.36	2.35	1.89	6.22	1.10	1.89	3.96	0.74	3.74	4.70
Miami sand, Ohio	.21	.51	1.52	.83	2.59	2.12	.34	1.21	.75	1.89	2.44	3.98
Wabash loam, Ohio	.11	.19	.40	1.56	1.56	3.98	.42	1.07	1.74	2.24	2.90	4.18
Volusia silt loam, Ohio	.09	.09	.46	.43	.30	.43	.37	.37	1.41	2.11	2.16	2.96
Marshall loam, Minnesota	.18	.19	.37	1.63	1.53	4.02	.61	1.30	1.73	1.97	1.71	1.02
Miami silt loam, Wisconsin	.12	.19	.56	.91	.83	1.37	.57	.50	1.73	2.07	2.44	3.73
Marshall silt loam, Wisconsin	.13	.24	.52	.76	.81	1.20	.46	.75	1.68	1.78	2.41	3.32
Marshall black clay loam, Illinois	.31	.32	.56	3.17	2.50	5.53	1.26	1.29	2.79	1.99	2.39	2.54
Marion silt loam, Illinois	.05	.08	.35	.38	.51	.88	.10	.14	.99	.94	1.44	2.07
Shelby silt loam, Missouri	.19	.16	.49	.41	.44	1.14	.13	.25	1.20	1.50	1.87	2.26

TABLE XIII.—*Content of the separates of the glacial soils calculated to percentages of the whole soil.*

Soil type and location.	P_2O_5.			CaO.			MgO.			K_2O.		
	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Podunk fine sandy loam, Connecticut	0.10	0.05	0.07	1.89	0.33	0.12	0.89	0.33	0.08	0.60	0.66	0.09
Miami sand, Ohio	.19	.03	.05	.76	.14	.07	.31	.07	.03	1.73	.13	.14
Wabash loam, Ohio	.06	.07	.05	.79	.59	.48	.21	.41	.21	1.13	1.10	.50
Volusia silt loam, Ohio	.02	.06	.09	.07	.19	.08	.06	.24	.27	.36	1.38	.56
Marshall loam, Minnesota	.09	.07	.05	.78	.58	.51	.29	.49	.22	.89	.64	.13
Miami silt loam, Wisconsin	.02	.14	.08	.12	.60	.19	.08	.36	.24	.28	1.76	.52
Marshall silt loam, Wisconsin	.02	.17	.09	.09	.57	.20	.06	.52	.29	.21	1.69	.56
Marshall black clay loam, Illinois	.07	.18	.11	.68	1.44	1.11	.27	.74	.56	.43	1.37	.51
Marion silt loam, Illinois	.01	.05	.06	.05	.35	.16	.01	.10	.18	.12	1.00	.37
Shelby silt loam, Missouri	.01	.12	.09	.03	.33	.22	.01	.19	.23	.11	1.38	.43

In general, the finer separates of the soils of this group contain the greater percentages of the several elements determined. The Marshall loam and the Volusia silt loam depart most widely from this rule, but several others do not strictly conform to it. The extreme proportionate richness of the clay of the Podunk fine sandy loam may have some connection with the great quantity of fertilizers that have been applied in the growing of tobacco on the field from which the sample was taken.

As to total content of the elements in the several separates, this is generally determined by the relative quantity of the separates in the soil. Thus in the soils consisting largely of silt, a large part of the phosphorus, calcium, magnesium, and potassium is contained in the silt. In the soils consisting largely of sand, the plant-food constituents are found in greatest quantity in the sand. As shown in Table XIII, the silt of Miami silt loam and of Marshall silt loam contains much more phosphate, lime, magnesia, and potash than is contained in the sand and clay combined. The sand of the Miami sand contains more of these elements than the combined content of the silt and the clay.

SOILS DERIVED FROM LIMESTONES AND SHALES.

Five soils formed from limestones and shales without glacial agency are included in this comparison—Oswego silt loam from Kansas; Wabash silt loam, Kansas; Hagerstown loam, Tennessee; Hagerstown clay, Kentucky; Houston clay, Alabama.

Oswego silt loam.—Described as Oswego loam in the report of soil survey of Parsons area, Kansas, 1903. This soil consists of a dark gray silty loam, varying from very shallow to 10 inches deep, which grades into a stiff clay, becoming more impervious with depth. It becomes hard and compact on drying, but it is easily broken up into a mellow loam if plowed when in proper condition of moisture. This is an upland type and occupies gently rolling prairies. Owing to the topography of the country, the type has good surface drainage. The Oswego silt loam is derived from the weathering of the underlying rock, this usually being shales, with occasional interbedded layers of sandstone and limestone.

Wabash silt loam.—The sample analyzed is from Riley County, Kans. The area was surveyed in 1906. The soil varies from 12 to 24 inches in depth and consists of a dark-brown to black heavy silt loam. It is easily cultivated and readily kept in good tilth. The subsoil consists of a compact and rather heavy brown or yellowish silt loam. It occurs as long, narrow tracts in the creek valleys and along the outer edges of the river valleys. The type occupies a rather low position in stream valleys and on gentle slopes. Its surface is nearly level or gently sloping. It forms first bottoms of smaller streams and second bottoms of larger ones. It is well drained naturally. The type has been deposited by water, the surface consisting largely of material washed from the surrounding hills, which are made up of shales and limestones. This wash from the hills is continually adding to the type.

Hagerstown loam.—Sample collected in the soil survey of the Pikeville area, Tennessee, 1903. This soil consists of brown or yellowish-brown mellow loam from 9 to 12 inches deep. It is underlain by a yellow to reddish-yellow stiff loam or light clay loam, which becomes a more pronounced red with depth. Traces of chert are found in both soil and subsoil. This type was formed by the slow weathering of limestones. In this soil the weathering has been so complete and the leaching so excessive that the lime of the disintegrated stone has been largely washed from the soil. The type has a moderately rolling surface and has good surface drainage, but the subsoil is rather impervious. The underlying limestone comes near the surface in some places, owing to erosion.

Hagerstown clay.—The sample analyzed was collected in the soil survey of Scott County, Ky., 1903. This soil has a heavy texture and varies from 3 to 12 inches in depth. It is yellow or brown in color. The subsoil is a heavy yellow clay, extending to a depth of 3 or more feet. This soil type is derived from limestones and shales. These rocks offer considerable resistance to disintegration, and the soil may therefore be more thoroughly leached than would be the case were the rocks more readily decomposed. The surface is rather rough, rounded hills being dominant features. Surface washing has been great, and the soil is generally shallow, the depth depending on its position. This is a residual soil, being formed from the breaking down in place of the underlying limestones and shales.

Houston clay.—The sample is from Dallas County, Ala. The area was surveyed in 1905. Although this type is really a Coastal Plains soil in so far as its mode of occurrence is concerned, it is here grouped with the limestone soils. It has resulted from the weathering of rotten limestones or chalks of Cretaceous time. Owing to its proximity to the soft and easily broken down lime rock, this soil is highly calcareous, and often contains lime concretions, especially in the subsoil. It may be considered to be of comparatively recent origin and as a residual Coastal Plains soil. The soil is a gray, brown, or black loamy clay, 6 inches deep. This is underlain with 3 or more feet of heavy gray or mottled yellow clay. The surface is gently rolling and the drainage very good. Agriculturally the soil is lighter than would be expected from its high clay content. This may be due to flocculation by the high percentage of lime present.

Table XIV shows the mechanical composition of the soils of this group. Tables XV and XVI give the results of the chemical examinations.

TABLE XIV.—*Mechanical composition of the soils formed from limestones and shales.*

Soil type and location.	2 to 0.05 mm. (sand).	0.05 to 0.005 mm. (silt).	0.005 to 0 mm. (clay).
	Per cent.	*Per cent.*	*Per cent.*
Oswego silt loam, Kansas	25	57	18
Wabash silt loam, Kansas	13	69	18
Hagerstown loam, Tennessee	36	40	23
Hagerstown clay, Kentucky	7	48	46
Houston clay, Alabama	28.5	25.5	46.5

TABLE XV.—*Partial chemical composition of the separates of limestone and shale soils.*

Soil type and location.	P_2O_5.			CaO.			MgO.			K_2O.		
	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Oswego silt loam, Kansas	0.07	0.08	0.31	0.19	0.33	0.93	0.06	0.13	1.54	0.64	1.31	1.88
Wabash silt loam, Kansas	.05	.07	.40	.81	.88	2.67	.30	.43	2.16	2.27	2.96	3.64
Hagerstown loam, Tennessee	.04	.05	.40	.22	.26	.94	.19	.30	1.60	.12	.84	1.68
Hagerstown clay, Kentucky	.32	.28	.55	7.81	3.12	2.37	.76	.87	2.32	3.48	3.60	5.07
Houston clay, Alabama	.48	.36	.77	28.73	29.51	26.45	.87	.88	1.60	.79	1.05	1.10

TABLE XVI.—*Content of the separates of the limestone and shale soils calculated to percentages of the whole soil.*

Soil type and location.	P_2O_5.			CaO.			MgO.			K_2O.		
	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Oswego silt loam, Kansas.	0.02	0.05	0.05	0.05	0.19	0.16	0.02	0.07	0.27	0.16	0.75	0.33
Wabash silt loam, Kansas.	.01	.05	.07	.10	.60	.48	.04	.29	.38	.29	2.03	.65
Hagerstown loam, Tennessee	.01	.02	.09	.08	.10	.22	.07	.12	.37	.04	.34	.39
Hagerstown clay, Kentucky	.02	.13	.25	.55	1.50	1.09	.05	.42	1.07	.24	1.73	2.33
Houston clay, Alabama	.14	.09	.36	8.19	7.53	12.30	.25	.22	.74	.23	.27	.51

Excepting the lime and the phosphates in the calcareous soils, Hagerstown clay of Kentucky and Houston clay of Alabama, these limestone and shale soils follow the rule that the finer the separate the greater the percentage of the four elements determined. In the cases of high lime content there may be calcium carbonate in the form of sand as that term is here used, and quartz and other sands may be coated with carbonate of lime. In the clay soils the greatest absolute quantity of lime is contained in the clays; in the loams the silts often have greater quantity.

The Oswego silt loam and the Hagerstown loam are in marked contrast with the clays in that the latter contain larger percentages of the several elements determined, notably the potash in Hagerstown clay, the lime in Houston clay, and the phosphoric acid in both. This comparative poverty in the former is doubtless due in part to these soils being the result of more extended weathering than are the two clays, and the rocks from which they are formed differ considerably.

While the separates of any one of these shale and limestone soils can be compared among themselves, no useful comparison of one of the soils with another can be made unless the full history of the soils be considered. Some of them have come from shales with layers of interbedded limestones, others from massive limestones, and the extent of weathering and leaching has varied so that a similar soil could not result. Notwithstanding this, the plant-food constituents are concentrated in the finer separates of all these shale and limestone soils as in those of greatly different origin.

Not only are the finer separates of this group of soils richer in plant-food constituents as determined by percentage composition, but since the soils are mainly clay and silt the absolute quantities, as shown by Table XVI, are greater in these portions.

SOILS OF THE ARID REGIONS.

Two soils formed under arid conditions, or at least that have been under arid conditions for very long periods, were used in this work—one from the Fresno series and one from the Indio series.

Fresno fine sandy loam.—Described as Fresno sandy loam in the report of the soil survey of the Fresno area, California, 1900. This soil is composed largely of silt to fine sand. It is locally known as "white-ash land," from its color and its physical character. The soil has probably been derived from volcanic ash, but light-colored loams and sands have also contributed to it. The soil lies flat and works well, unless it be puddled, when water penetrates it slowly and hard clods or lumps form on drying. The lower subsoil is heavier, a blue clay being encountered at the depth of a few feet. Because of poor drainage or light rainfall this soil generally contains alkali.

Indio fine sandy loam.—Described as Fresno sandy loam in the report of the soil survey of the Indio area, California, 1903. This soil is made up of clay, silt, and the finer grades of sand. The clay is so flocculated that the soil in its field condition is lighter than the mechanical composition would indicate. The soil was mainly formed by erosion from adjacent mountains, the material being deposited in a bay or arm of the sea, but it has been greatly modified by wind action. It contains micaceous grains and minute shells. The soil ranges in depth from 2½ to 5 feet and is underlain with sandy loam or sand. The surface usually has a uniform slope and is generally well drained, but its high capillary power draws much water to the surface, causing an accumulation of alkali by its evaporation. In the lower levels the alkali is present in injurious amounts. Owing to insufficient rainfall the salts are not washed out of this soil so well as might be expected from its physical character.

Tables XVII, XVIII, and XIX give the mechanical composition and the results of the analysis of the separates of these soils.

Table XVIII would show these two soils to be somewhat similar to those of humid regions in respect to the distribution of the elements in the mechanical separates. Excepting the lime in the highly calcareous Indio fine sandy loam, the finer the separates, in general, the higher the percentage of the elements determined, and of course the less siliceous they are. Since these soils contain considerable alkali or water-soluble salts, constituents which would here appear in the clay, the content of the clay proper would be somewhat less than shown in the tables. In the case of the potash it would probably be considerably less. It will be observed that the sand of the Indio fine sandy loam contains slightly more potash than the silt. Were the apparent content of potash in the clay reduced by that which has been washed from the whole bulk of soil and concentrated in the clay, thus obtaining that of the clay itself, this true content would probably not greatly exceed that of the sand. Were the same correction made for the Fresno fine sandy loam, the clay would be about like the silt in potash content. The same considerations apply to the other elements, but doubtless to a less degree; but after making due allowance for this source of error, it would appear that the coarser particles are somewhat poorer in phosphorus, magnesium, and potassium.

TABLE XVII.—*Mechanical composition of the arid soils.*

Soil type and location.	2 to 0.05 mm. (sand).	0.05 to 0.005 mm. (silt).	0.005 to 0 mm. (clay).
	Per cent.	*Per cent.*	*Per cent.*
Fresno fine sandy loam, California	66.5	25.5	8
Indio fine sandy loam, California	46	29	24

TABLE XVIII.—*Partial chemical composition of the separates of the arid soils.*

Soil type and location.	P_2O_5.			CaO.			MgO.			K_2O.		
	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Fresno fine sandy loam, California	0.15	0.22	0.65	3.16	3.55	6.20	0.78	1.81	5.85	3.26	5.58	6.27
Indio fine sandy loam, California	.22	.27	.25	15.02	14.89	9.87	2.20	4.14	4.82	2.84	2.73	2.86

TABLE XIX.—*Content of the separates of arid soils calculated to percentages of the whole soil.*

Soil type and location.	P_2O_5.			CaO.			MgO.			K_2O.		
	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.	Sand.	Silt.	Clay.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Fresno fine sandy loam, California	0.10	0.06	0.05	2.10	0.91	0.50	0.52	0.46	0.47	0.17	1.42	0.50
Indio fine sandy loam, California	.10	.08	.06	6.94	4.35	2.36	1.02	1.21	1.15	1.30	.80	.92

COMPARISONS OF THE GROUPS OF SOILS.

It is interesting to compare the soils of one province with those of another. If the soils of the Coastal Plains be compared with those of the Piedmont Plateau and of the Appalachian Mountains, certain distinct differences are observed. The latter soils are residual—that is, they have been formed where now found or have been moved but short distances. The method of formation, in addition to pulverization, has been one of removal of certain parts of the rocks, either by solution or, mechanically, by moving water or air, leaving the present soil as a residue. The material forming the soil may differ but little chemically and mineralogically from the rocks whose breaking down has produced the soil, or it may depart much from them. An illustration of the latter is seen in the clays resulting from limestones.

The soils of the Piedmont used in this investigation contain abundant fragments of the original minerals undecomposed. The Coastal Plains soils have resulted to a large extent from material washed from the Piedmont Plateau and deposited in water at lower levels.

They have suffered from decomposition and solution more than have the Piedmont and Appalachian soils, and there has often been a greater separation of the finer from the coarser particles.

The tables show that the residual soils, Chester mica loam, Porters black loam, and Cecil clay, contain more plant-food constituents than do the Coastal Plains soils. This is especially true of the phosphorus, the potassium, and the magnesium. It is in the coarser materials, the sands, where the greatest difference in composition is found. In the sands of the residual soils the potash averages 1.60 per cent, in the sands of the Coastal Plains soils the potash averages 0.37 per cent, the sands of the residual soils being over four times as rich. In the clays the averages are, respectively, 2.86 per cent and 1.79 per cent, the clays of the residual soils being about one and a half times as rich as those of the Coastal Plains soils. A comparison of the potash content of the sand of a soil with that of the clay of the same soil shows that relatively as well as absolutely the sands of the residual soils are richer than those of the Coastal Plains. For example, in the Norfolk loam and the Crowley silt loam, having the least difference in the potash content of the sand and the clay of any of these Coastal Plains soils, the clay is three times as rich as the sand. In the Orangeburg fine sandy loam the content of potash in the clay is seven times that in the sand. In the Orangeburg sandy loam the ratio is 30 to 1. In the residual soils, on the other hand, the ratios are smaller, being 2.7 to 1 in Porters black loam, 1.8 to 1 in Chester mica loam, and 0.7 to 1 in Cecil clay. A similar comparison for the other elements will lead to the same conclusion—that the clays and the sands of the Coastal Plains soils differ more in composition than do those of residual soils.

The glacial soils consist largely of crushed rocks. Much of the material composing them has not been profoundly weathered. They are therefore quite similar in composition to the residual soils, and hence differ from those of the Coastal Plains. A comparison of the composition of the separates of glacial, residual, and Coastal Plains soils shows this. It is true of all constituents, unless it be phosphorus. If, as before, the potash content be taken for comparison, it is seen that the clays of the glacial and the residual soils contain about twice the percentage that the sands do, while the potash content of the clays of the Coastal Plains soils is five times that of the sands.

The sandy and the silty glacial soils are somewhat similar in percentage composition. Owing to the latter consisting to so large an extent of such fine particles, it might have been supposed that decomposition and leaching would have affected them more, and that there would have been a greater difference between the two classes than the figures show. The average potash content of the silty soils is slightly greater than that of the others, as may be determined from the table, being 2.16 per cent and 1.94 per cent, respectively. The magnesia is 0.74 per cent of the silty soils and 0.86 of the others; the lime, 1.08 per cent and 1.76 per cent; the phosphoric acid, 0.23 per cent and 0.22 per cent, the figures being in all cases averages calculated from the table. But the silty soils are loessial for the most part and were formed from material blown by winds from glaciated areas and deposited where now found, or of material that has since been reworked by water. Minerals rich in alkalies and alkaline earths, being relatively easily crushed, would form a larger percentage of these silty soils than they do of the original glacial soils; so that even if there has been a tendency to impoverish them by leaching, their originally greater richness enables the loessial soils to compare well with those strictly glacial.

We have but two soils of the arid region to compare with the twenty-five of humid regions. The latter were selected to represent soils of all classes—those of low, of medium, and of high productivity; sandy soils, clay soils, calcareous soils, and those intermediate between these several extremes. They may be taken as fairly well representing the humid soils. The two arid soils can not be considered to represent so well those of the region because of their limited number and similarity of texture, both being fine sandy loams.

If the separates of these arid soils be compared with those of soils that have been profoundly weathered and leached, such as the Coastal Plains soils and the shale soils, it will be found that the coarser separates of the former are richer relatively than the finer ones. If a like comparison be made of the arid soils with the glacial soils, the residual soils, and the calcareous soils, they are all found to be quite similar in so far as the distribution of nutrients among the separates is concerned.

It should be noted that our comparison of arid soils with those of humid regions is in no way similar to that made by Tolman (p. 10). He compared the solubility of the separates rather than their composition. It is well known that sands are often coated with colored iron compounds, so that what is called a yellow or a red sand becomes transparent, colorless quartz sand when treated with acid. Other minerals in the form of sand are also similarly coated. The finer portions, the silts and the clays, are often the most highly colored. It is generally impossible to tell whether the coloring compounds are simply finely pulverized and mixed with the silt and the clay, or whether the colors exist in the form of thin coatings on the grains of these materials. Schloesing[a] believes the latter to be largely the case. It seems reasonable to believe that the slightly soluble compounds existing in soils, such as the carbonates and the phosphates of the alkaline earths, the phosphates of iron and aluminum, the more soluble silicates and silico-aluminates, etc., may form coatings on minerals just as do the oxides and the hydroxides of iron. If the minerals or their decomposition products had been in solution and then separated out because of concentration of the solution by evaporation, the deposition would be on the grains. Even if the adhesive force were equal over surfaces of large and of small grains, so that the films would be of equal thickness, there would be a larger percentage in the coatings of small particles, since in these the surfaces exposed are much greater in proportion to mass. There would be a tendency for this coating film to thicken, for on the assumption of a surface attraction, it would be from the reserves of these slightly soluble substances and not from the films that more of the material would go into solution when water is added to the soil by rain or otherwise. The deposition would take place over the previous film as the soil becomes drier again. At length the action would be in equilibrium when the tendency to dissolve from the films and from the reserves is equal. While this is probably one of the reasons for the greater percentage of acid-soluble substances in the finer separates, it can hardly be doubted that because of their softness in comparison with such minerals as quartz the compounds containing the nutrients are more finely pulverized in soil making, and that they are therefore more largely reduced to the size of silt and clay. In arid regions this solution and deposition would not take place to so large an extent, since the soils are seldom thoroughly wet. Decomposition or alteration taking place on the surfaces of mineral grains, the latter would remain coated with decomposition products if there were lack of water to remove the coating or to continue the kaolinization process further. The coarser grains of soils are more likely to be thus coated in arid regions than in humid ones. The decomposition products being more soluble in acid than the original minerals, it may frequently happen that the sands of arid soils yield more material to the acid used in analysis than do the sands of humid soils, and for the reason given above. Tolman[b] believes this to be a general fact, and suggests the above explanation of it.

While the existence or nonexistence of these unremoved coatings of decomposition products would account for differences in the solubility of the mechanical separates of soils, they would cause no great difference in composition as shown by fusion methods, for the latter would show the total content of the grains, whether they be partially decomposed or not.

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[a] Compt. Rend., **135**, 601–605 (1902).

[b] Rept. Agr. Expt. Sta., Univ. Cal., 1898–1901, p. 40 et seq.

ROCKS, SOILS, AND SOIL SEPARATES.

Comparisons have often been made of residual soils with the rocks from which they were in large part formed. In many cases this can be done with considerable certainty that the proper materials are being compared. But most of the soils studied in this bulletin are far removed from the rocks whose disintegration produced them, and they are mixtures of such diverse materials that comparisons of the sediments with the parent rock can not be made. It may, however, be of interest to compare the separates of these soils with such well-known rocks as granites, syenites, gneisses, shales, and sandstones. Each of these classes of rocks varies considerably in ultimate composition, depending upon the proportion of their constituent minerals, but by taking several of each class some conception of common limits of variation may be formed. In the following tables the percentages of P_2O_5, CaO, MgO, and K_2O in a number of these rocks are given.[a]

TABLE XX.—*Partial composition of granites.*

Type of rock and location.	P_2O_5.	CaO.	MgO.	K_2O.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Granite, Currant Creek Canyon, Pikes Peak, Colorado	0.22	0.58	0.07	6.56
Biotite granite, Sentinel Point, Pikes Peak, Colorado	Trace.	.80	.04	4.92
Granite, Currant Creek Canyon, Pikes Peak, Colorado	.05	.23	.14	7.99
Biotite granite, Vermont	.11	1.13	.33	4.81
Soda granite, Minnesota	.20	.66	.58	4.97
Granite, Florissant, Colorado	Trace.	.15	Trace.	4.15
Granite, Montana	.06	1.26	.35	6.09
Aplite, Sierra County, California	.03	1.28	.05	5.18

TABLE XXI.—*Partial composition of trachyte-syenite rocks.*

Type of rock and location.	P_2O_5.	CaO.	MgO.	K_2O.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Nordmarkite, Vermont	0.13	1.49	0.40	5.97
Quartz syenite porphyry, Bearpaw Mountains, Montana	.10	1.32	.77	5.76
Biotite trachyte, Dike Mountains, Yellowstone National Park	.22	.93	.63	5.47
Soda syenite porphyry, Moccasin Creek, California	.11	.55	.24	.10
Soda syenite, Alaska	.06	2.66	.06	.39
Biotite trachyte, Dike Mountains, Yellowstone National Park	.25	2.78	.91	6.11
Augite syenite porphyry, Copper Creek Basin, Yellowstone National Park	.21	2.60	1.13	4.56
Augite syenite, Turnback Creek, California	.16	5.61	1.69	7.70
Syenite, Little Belt Mountains, Montana	.33	4.61	3.67	4.50
Syenite, Colorado	.35	3.77	1.24	5.05
Syenite, Crazy Mountains, Montana	.26	3.69	1.51	5.34

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[a] Clarke. Data of Geochemistry, 368–371, 463, 468, 534–535 (1908).

TABLE XXII.—*Partial composition of gneiss.*

Type of rock and location.	P_2O_5.	CaO.	MgO.	K_2O.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Sedimentary gneiss, Canada	....	0.35	1.81	2.50
Quartz-biotite-garnet gneiss, New Nork	0.11	2.40	2.40	1.93
Mica gneiss, Pennsylvania	.22	1.87	2.42	2.86
Gneiss, Maryland	....	9.69	5.98	1.56
Gneiss, sedimentary, Great Falls Potomac	.11	1.68	.95	1.35
Biotite gneiss, Michigan	....	1.87	1.26	2.35
Quartz-norite gneiss, Minnesota	....	5.99	3.62	.55

TABLE XXIII.—*Partial composition of sandstones.*

Type of rock and location.	P_2O_5.	CaO.	MgO.	K_2O.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Brown sandstone, Hummelstown, Pa	....	0.20	0.53	2.63
Ferruginous sandstone, Norfolk, England	0.42	2.43	.95	.48
From a "Sandstone dyke," Shasta County, Cal	.14	16.39	2.22	1.17
Miocene sandstone, Mount Diablo, Cal	.29	14.65	5.55	1.37
Composite of 253 sandstones	.08	5.52	1.17	1.32
Composite of 371 building sandstones	.06	1.05	.52	1.16
Sandstone from Hurley, Wis	....	.70	1.39	1.62

TABLE XXIV.—*Partial composition of shales.*

Type of rock and location.	P_2O_5.	CaO.	MgO.	K_2O.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Composite of 51 Paleozoic shales	0.15	1.41	2.32	3.60
Composite of 27 Mesozoic and Cenozoic shales	.20	5.96	2.67	2.07
Black Devonian shale, Morenci, Ariz	.08	3.40	4.16	6.74
Middle Cambrian shale, Coosa Valley, Alabama	.06	1.60	2.32	3.19
Bituminous shale, Dry Gap, Georgia	.31	.78	1.15	3.16
Shale near Rush Creek, Colorado	.17	12.09	2.12	2.31
Carboniferous shale, Elliott County, Ky	.08	9.91	1.91	.88
Cretaceous shale, Mount Diablo, California	.08	27.87	2.61	....

A comparison of the figures in the above tables with those for the separates of the glacial soils in Table XII shows that the phosphates in these rocks and in the sands and silts are of about the same order of magnitude, and that they are appreciably higher in the clays. It would seem, then, that in so far as these soils resulted from rocks like the above there has been little change in the percentage of phosphates in the portions forming sand and silt, while there has been a concentration in the clays. The change of the minerals comprising these rocks to "clay" is a somewhat complex one. In so far as it is chemical it is mainly a loss of alkalis and alkaline earths by solution, and the taking up of water in kaolinization. The first process would tend to increase the proportion of phosphate, the latter to decrease it.

A similar comparison of the lime content shows that, while there is much variation in the percentage of this base, in general the granites are somewhat below and the syenites and gneisses somewhat above the several separates.

The sands and the silts of the glacial soils have much the same magnesia content as the granites and syenites, and the clays are richer. The gneisses contain more magnesia than any of these separates.

A comparison of the potash content shows that the granites and syenites are richer in this element than are any of the sediments—much richer than the sands and the silts. The gneiss rocks are about like the sands and poorer than the silts and clays.

These various relations may have come about by the mixing of the débris of very diverse rocks, those richer in the elements named with those poorer, or by the decomposition and leaching of the broken down richer rocks.

Of the soils formed from crystalline and metamorphic rocks by other than glacial action (pp. 19 to 21) the Chester mica loam and the Cecil clay, as a whole, contain about the same proportion of phosphate as do the granites and gneisses, the sands and silts being low, the clays relatively high. Calcium is a less abundant constituent of the soils than of the rocks. The soils contain about as large a proportion of magnesium as the granites and less than the gneisses. The syenites are variable in the content of this element, some of these rocks being poorer than the two soils and some richer.

Some of the separates of these soils are richer in the elements than the rocks and some poorer. Thus in general the rocks contain a greater percentage of phosphate than the sand and silt separates and less than the clays. All the separates are of lower lime content than the rocks. Their magnesia content is greater than that of the granites and less than that of the gneisses. The potash of the separates is very similar to that of the gneisses, but much less than that of the granites.

Porters black loam more nearly resembles the syenites in composition, and its separates are irregular when compared with the rocks. This soil is said to be derived from granites and gneisses in large part. The content of potash, lime, and magnesia in the whole soil is intermediate between that of the rocks as shown in these tables.

SUMMARY.

As a general rule the smaller particles of soils are richer in potassium, calcium, magnesium, and phosphorus than the coarser particles.

The concentration of these elements in the finer components is the more pronounced as the soils have undergone more extreme weathering.

In glacial soils and others resulting largely from mechanical processes the coarser particles are relatively high in the percentages of potash, lime, and magnesia.

The larger mechanical components contain these elements in forms which by protracted weathering will become more soluble, and they will ultimately be concentrated in the finer components.

Calcium is often rather low in clay soils resulting from the weathering of hard, compact limestones. It is generally abundant in soils recently formed from easily broken down limestones. The sands of these latter soils may contain a high percentage of calcium, probably as lime sand or as coatings on other large mineral grains.

A comparison of soils and soil separates with crystalline rocks indicates that in the process of the weathering of these rocks the phosphate remains of about the same proportion or slightly increases. The lime and potash seem to decrease in percentage, although minerals containing them are always present.

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